Modified Statistical Method to Calculate Rare Gas Interaction Potentials

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ABSTRACT

New density functionals representing the exchange and correlation energies (per electron) are employed, based on the electron gas model, to calculate interaction potentials of noble gas systems X_2 and XY, where X (and Y) are He,Ne,Ar and Kr, and of hydrogen atom-rare gas systems H-X. The exchange energy density functional is that recommended by Handler and the correlation energy density functional is a rational function involving two parameters which were optimized to reproduce the correlation energy of He atom. Application of the two parameter function to other rare gas atoms shows that it is "universal"; i.e., accurate for the systems considered. The potentials obtained in this work compare well with recent experimental results and are a significant improvement over those from competing statistical models.

CHAPTER I

INTRODUCTION

Intermolecular forces (IMF) between closed-shell atoms and molecules afford us an understanding of a great variety of phenomena such as; the geometry and stability of molecular solids, properties of liquid and phase transistions, collisions between molecules in gases and in molecular beams and others.[1]

Although direct calculation of the forces is very complicated (especially when the number of electrons involved increases) there are no conceptual difficulties. In principle, the IMF could be calculated starting from the knowledge of fundamental constants and the Schrödinger equation. Such ab initio calculations, however, become expensive when large systems are considered. In fact, calculations which include extensive correlation have been carried out only for systems with few electrons such as He-He. And even for this system, there is still an uncertainty of about 5 per cent in the depth of the potential well.[2]

Other theoretical methods[1,3] yield good results only in the short- and long-range regions of the potential curve. Self-consistent field (SCF) calculations with or without limited configuration interaction (CI) appear to give accurate results for small internuclear distances (R). The computation involved here however, is very lengthy in that an SCF or CI calculation has to be repeated at every R, not to mention the complexity when heavier systems are involved. In the long-range region (R is big), where the interaction energy is very

small compared to the total energy, variational calculations bog down. This is because, in such regions, the energy of the molecular system is comparable to the sum of the energies of the isolated atoms, thus magnifying the errors inherent in the model. Hence, perturbation theory is used for the long-range interaction. Here the interaction energy V_{disp} can be expressed in the form that depends only on R. This interaction is dominated by the correlation or dispersion effects (see Chapter II Section B3). However, the perturbation method is poor at short and intermediate distances since interatomic electron exchange and electron density overlap are not taken into account. Also, the perturbation series diverges when the interaction is strong, that is when R approaches a small number.

In the region of greatest interest, the intermediate region, the above methods do not give satasfactory results. For systems that do not form a strong chemical bonds, for example, rare gases, SCF calculations predict repulsion with no potential minimum while dispersion or perturbation theory predicts attraction but also without a potential minimum (see Fig. 1). It requires a very careful and elaborate CI to successfully yield the potential well, and it is questionable given present technology if such an elaborate method can be applied to more complex systems. Because of these difficulties an understanding of IMF by theoretical studies is lacking. Therefore, in the construction of the potential curves for a large number of systems, experimental results of beam scattering, virial and transport coefficient measurements, and liquid and solid state properties, etc., are used.[4]

A simple statistical method which is capable of giving reliable

Fig. 1 Self-consistent field (SCF) and long-range perturbation calculations for Ar_2 ($^1\Sigma_g^+$).

The solid line is from the ab initio calculation of T.L. Gilbert and A.C. Wahl, Journal of Chemical Physics 47, 3425 (1967). The broken line represent the dispersive energy due to Tang and co-workers (reference 24) for C_6,C_8,C_{10} and due to Rae (reference 8) for C_{12} and C_{14}.

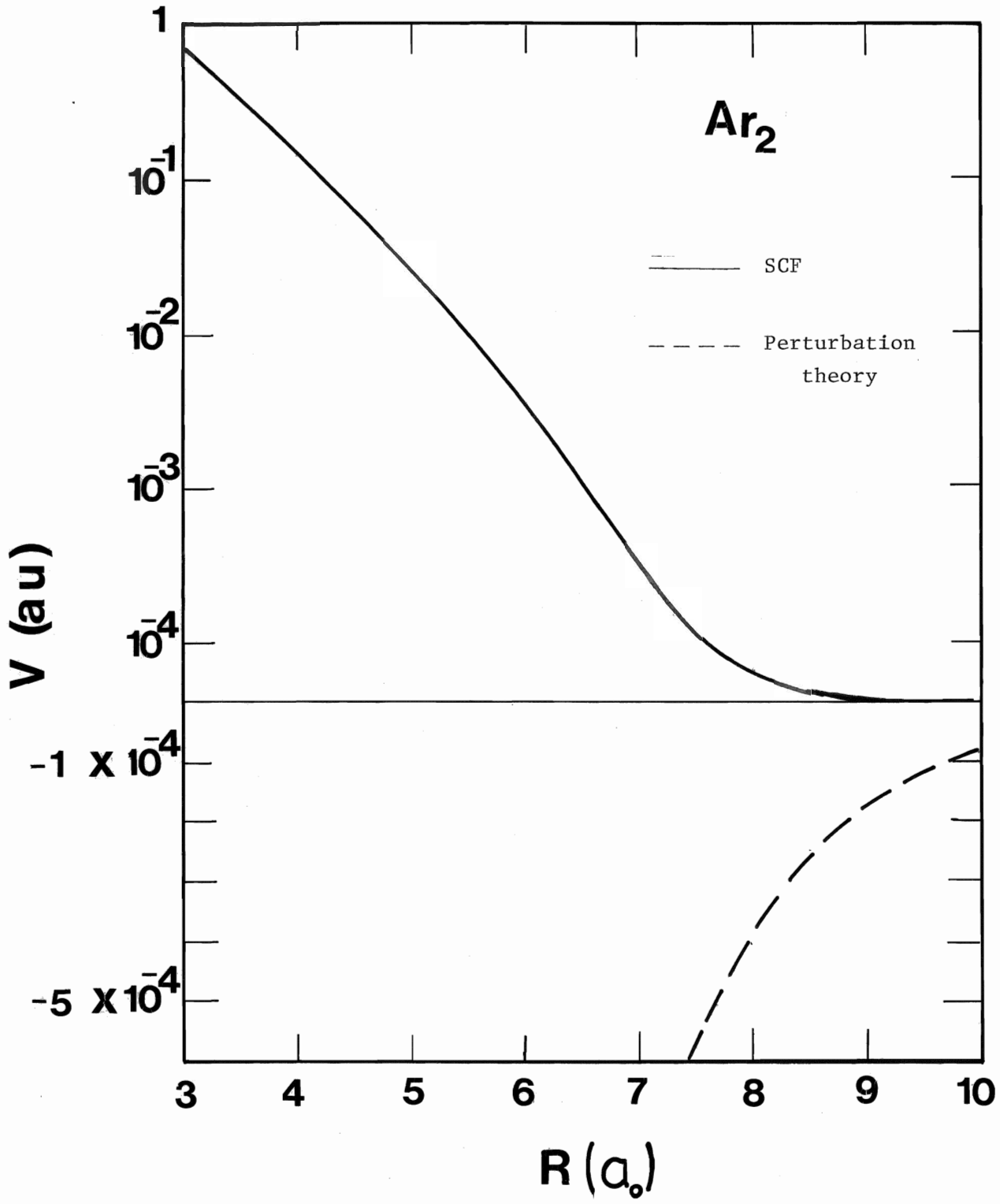
Ar2
SCF
Perturbation theory
V (a u)
1
10-1
10-2
10-3
10-4
-1 x 10-4
-5 x 10-4
3
4
5
6
7
8
9
10
R (ao)

Fig. 1

repulsive potentials has been developed by Gaydaenko and Nikulin[5] and by Gordon and Kim[6]. In this method, the principal assumption is that the distribution of electron density of the two atoms as they interpenetrate is not distorted, thus the density at any point in the molecular system can be taken as the sum of densities associated with the separated atoms. The validity of this main assumption is reasonable only for the study of systems which do not form strong chemical bonds like closed-shell atoms,ions and molecules. For He-He system, the total density everywhere is within less than about ten per cent of the sum of atomic densities.[7]

Recently, important modifications to the above statistical model that give reasonably accurate potentials have been suggested by Rae[8] and by Cohen and Pack.[9] Rae found a way of correcting the exchange energy to account for too much binding for systems with small numbers of electrons. Cohen and Pack used the same approach, using as a parameter the total number of electrons of the system instead of the number of electrons in the valence shell of the atoms. Both methods incorporate the dispersive energy smoothly at all internuclear separations.

In this work, improved estimates for the exchange and correlation components of the interaction potential are proposed. Handler's[10] expression for exchange energy, which arises by imposing a positive definite Hermitian single particle density matrix in the Thomas-Fermi theory, is used. For the correlation energy , a rational function involving two parameters is suggested.

In chapter II, the usual statistical method is presented in detail together with our modifications to it. Equations involved are

presented, derivations of which are given in the Appendices.

In chapter III, the proposed statistical method is applied to rare gas diatomic systems X-Y, where X or Y can be He,Ne,Ar or Kr. Comparison with other approaches and the experiments for both like and unlike atoms are presented through tables and curves. The results as reported indicate overall improvement for the systems considered.

The applicability of the method to Hydrogen atom-rare gas system is explored in chapter IV.

Chapter V gives the summary and conclusions. Here, limitations and difficulties that may be encountered are also discussed.

C H A P T E R II

THE INTERACTION ENERGY

At a given internuclear separation R, the interaction energy V(R) is given by

$$V(R) = E(R) - E(\infty), \qquad \text{(II-1)}$$

where E(R) is the total energy of the system at R and $E(\infty)$ is the sum of the energies of the constituent atoms. Equation (II-1) can be written as

$$V(R) = V_{HF}(R) + V_{corr}(R), \qquad \text{(II-2)}$$

where $V_{HF}(R)$ is the Hartree-Fock energy and $V_{corr}(R)$ is the correlation energy.

Gordon and Kim (GK) approximate V_{HF} by

$$V_{HF} = V_c + V_k + V_e, \qquad \text{(II-3)}$$

where the three terms are the Coulombic, kinetic and exchange energy contributions respectively. All these terms are dependent on the electron density.

In the GK approximation, it is assumed that no rearrangement or distortion of atomic densities occurs when the atoms are brought together. Thus, for rare gas systems, the total electronic charge density ρ_{XY} would be the sum of the atomic densities ρ_X and ρ_Y, at each point in space:

$$\rho_{XY} = \rho_X + \rho_Y \ . \qquad \text{(II-4)}$$

For the description of the electron densities associated with the separate atoms, the Hartree-Fock wavefunctions by Clementi[11] are used. (Although more accurate wavefunctions could be employed for He,

they are not available for larger atoms.) Electron densities obtained from Hartree-Fock wavefunctions are accurate. For example, the result of electron diffraction data for Argon compares very well with the radial electron density calculated by the Hartree-Fock method.[12] Hartree-Fock (HF) density for a closed-shell atom is easily calculated:

$$\rho(r) = 2\sum_{occ.} \phi^*_{occ.}\phi_{occ.} \qquad \text{(II-5)}$$

where the ϕ's are the orbital wavefunctions and the summation extends over the occupied orbitals. From the addition theorem of spherical harmonics, it is evident that the density for a closed-shell atom would be spherically symmetric. In the following sections, the evaluation of all the terms in (II-2) and (II-3) is described in detail.

A. Coulombic Energy (V_c)

Within the Gordon and Kim approximation, the Coulombic energy is calculated directly from

$$V_c = \iint \rho_X(\vec{r}_1)\rho_Y(\vec{r}_2)(1/R + 1/r_{12} - 1/r_{1Y} - 1/r_{2X})d\vec{r}_1 d\vec{r}_2. \qquad \text{(II-6)}$$

After some manipulation, (cf. Appendix A) (II-6) becomes

$$V_c = \int_0^\infty 4\pi r_1^2 \rho_X(r_1)dr_1 \int_0^\infty 4\pi r_2^2 \rho_Y(r_2) I(r_1,r_2)dr_2 \ , \qquad \text{(II-7)}$$

where

$$I(r_1,r_2) = 1/R + F(R,r_1,r_2) - 2/(R+r_1+|R-r_1|) - 2/(R+r_2+|R-r_2|) \qquad \text{(II-8)}$$

and

$$F = 2/(R+r_1+|R-r_1|) \quad \text{for } r_2 < |R-r_1|, \qquad \text{(II-9a)}$$

$$= (1/r_1 + 1/r_2)/2 - R/4r_1r_2 - (r_1-r_2)^2/4Rr_1r_2$$

$$\text{for } |R-r_1| < r_2 < (R+r_1) , \qquad \text{(II-9b)}$$

$$= 1/r_2 \qquad \text{for } r_2 > (R+r_1) \qquad \text{(II-9c)}$$

For the homonuclear case, (II-8) by symmetry, could be reduced to

$$I(r_1,r_2) = 1/R + F(R,r_1,r_2) - 4/(R+r_1+|R-r_1|). \qquad \text{(II-10)}$$

The double integral in (II-7) is evaluated numerically by Gaussian quadratures. For the r_1 integral, it is found that optimal convergence is obtained if the $[0,\infty)$ domain is divided into three regions; $[0,2]$, $[2,4]$, and $[4,\infty)$. On the other hand, the integration over r_2 is best accomplished if the domain is divided into the three suggested by (II-9): $[0,|R-r_1|]$, $[|R-r_1|, R+r_1]$ and $[R+r_1,\infty)$. The regions with finite limits are computed using a 24-point Gauss-Legendre quadrature, following the scheme of McLean and Yoshimine[13]. Those with an infinite upper limit are done using a 24-point Gauss-Laguerre quadrature.

B. The Interatomic Interaction Energy.

The remaining terms in (II-3), the kinetic and exchange energies, and the correlation contribution in (II-2) are calculated by GK via the electron gas model. In this section, analyses of the traditional expressions and our modifications to them are presented.

1. The kinetic energy.

The expression for the kinetic energy follows directly from that of a uniform electron gas and is given by

$$V_k(GK;R) = \int \left[\rho_{XY}(\vec{r})\varepsilon_k(\rho_{XY}) - \rho_X(\vec{r}_X)\varepsilon_k(\rho_X) - \rho_Y(\vec{r}_Y)\varepsilon_k(\rho_Y)\right] d\vec{r} \ , \qquad \text{(II-11)}$$

where

$$\varepsilon_k(GK;\rho) = (3/10)(3\pi^2)^{2/3}\rho^{2/3} \ . \text{ (cf. Appendix B)} \qquad \text{(II-12)}$$

In this approximation, the local electron density is considered uniform, which is not a good supposition near the nucleus, where the actual density is rapidly varying. However, in rare gas systems, only the outer regions of the atoms, where the atomic densities overlap, give the major contribution to the interaction energy. Furthermore, when the atomic energies are subtracted from the total energy as in (II-11), the contribution of the nuclear regions, where the density varies, cancels out.

Shih[14] in a recent study of neutral atoms, includes Weisäcker's[15] inhomogeneity correction multiplied by a factor of 1/9. For most of the atoms considered, he obtained agreement with HF expectation values to better than one per cent, with the largest disagreement being 1.7%.

When Shih's correction is applied to the He_2 system, Eq. (II-11) becomes negative at all R, as given in Table 1. To understand the deficiency of this correction, Helium atom is investigated in detail. Employing a spherical coordinate system, the correction is written as

$$\text{Grad} = 4\pi\int_0^\infty r^2\left[\ \{1/9\}\ F(\rho)\ \right]dr\ , \qquad \text{(II-13)}$$

where

$$F(\rho) = (1/8)(|\nabla\rho|^2/\rho)\ . \qquad \text{(II-14)}$$

The true correction to the kinetic energy is easily determined by

$$\text{CHFKE} = 4\pi\int_0^\infty (\text{HFKE} - \text{UKE})r^2dr\ , \qquad \text{(II-15)}$$

where

$$\text{HFKE} = \psi^*_{He}(-\nabla^2/2)\psi_{He} \qquad \text{(II-16)}$$

and

$$\text{UKE} = \varepsilon_k\rho_{He}^{5/3}\ . \qquad \text{(II-17)}$$

With the aid of a 24-point Gauss Legendre quadrature, the terms in the integrals of (II-13) and (II-15) are plotted versus the density (ρ) in Fig. 2. Now it is evident that Shih's correction term (II-13) gives a completely erroneous description of the kinetic energy at each point in space, even though upon integration over all space, a reasonably accurate value for the kinetic energy is obtained. Thus when applying this correction to the He_2 system, it is not surprising that an incorrect result, negative kinetic energy in this case, is obtained.

Table 1. Electron gas kinetic energy and the inhomogeneity correction in He_2 ($^1\Sigma_g^+$) .[a]

R	Electron Gas Kinetic Energy[b]	Inhomogeneity correction[c]
1.0	0.1047 D 1[d]	-0.8793 D -1
1.5	0.4329 D 0	-0.6882 D -1
2.0	0.1648 D 0	-0.4467 D -1
2.5	0.5993 D -1	-0.2663 D -1
3.0	0.2117 D -1	-0.1517 D -1
3.5	0.7334 D -2	-0.8418 D -2
4.0	0.2505 D -2	-0.4594 D -2
4.5	0.8467 D -3	-0.2479 D -2
5.0	0.2840 D -3	-0.1327 D -2
5.5	0.9468 D -4	-0.7058 D -3
6.0	0.3142 D -4	-0.3737 D -3
6.5	0.1039 D -4	-0.1971 D -3
7.0	0.3430 D -5	-0.1036 D -3
7.5	0.1130 D -5	-0.5433 D -4
8.0	0.3724 D -6	-0.2842 D -4
8.5	0.1227 D -6	-0.1484 D -4
9.0	0.4048 D -7	-0.7740 D -5
9.5	0.1339 D -7	-0.4032 D -5
10.0	0.4441 D -8	-0.2099 D -5

[a] All values are in atomic units.

[b] Evaluated from Eqs. (II-11)and (II-12).

[c] Evaluated from Eq. (II-11) with ε_k equal to 1/9 of Eq. (II-14)

[d] 0.1047 D 1 is the same as 0.1047×10^1 .

Fig. 2 Behavior of the Weisäckers' correction and the true correction to the kinetic energy of Helium atom at different values of the density (ρ).

In the Y-coordinate of Fig.2, W_i and r_i pertain to the weight factors and the zeros of Legendre polynomials for the 24-point Gauss Legendre quadrature. For the true correction to the kinetic energy (solid curve), Y(r) equals (HFKE - UKE), which are the equations (II-16) and (II-17) respectively. For the Weisäckers' correction (broken line) Y(r) is just 1/9 of (II-14).

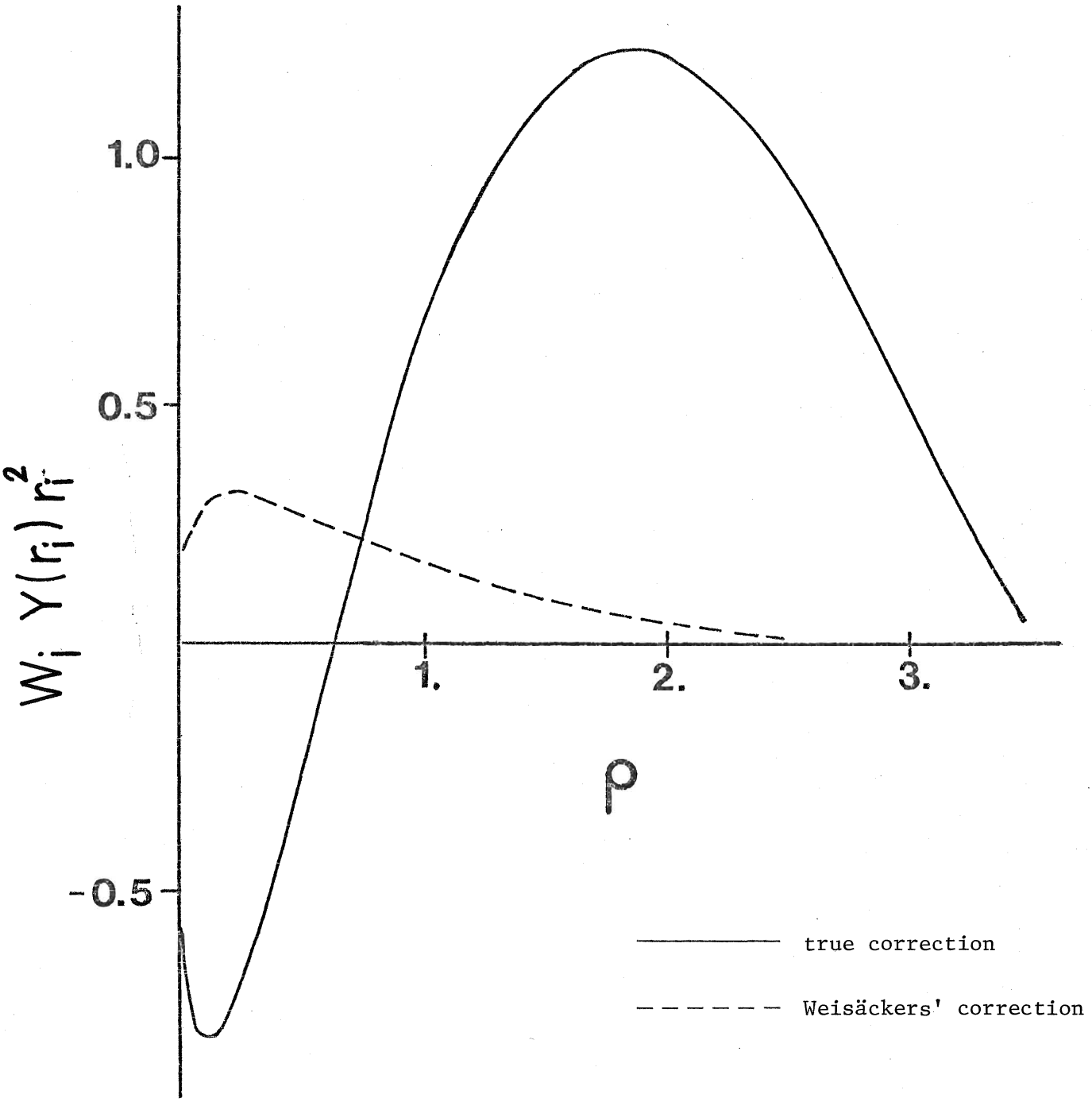

Fig. 2 Behavior of Weisäckers' correction and the true correction to kinetic energy (Helium atom) at different values of the density (ρ).

2. Exchange energy.

The standard GK expression for the exchange energy based on a uniform electron gas model is given by

$$V_e(GK;R) = \int [\rho_{XY}(\vec{r}_{XY})\varepsilon_e(GK;\rho_{XY}) - \rho_X(\vec{r}_X)\varepsilon_e(GK;\rho_X) - \rho_Y(\vec{r}_Y)\varepsilon_e (GK;\rho_Y)]\, d\vec{r} \,, \qquad \text{(II-18)}$$

where

$$\varepsilon_e(GK;\rho) = -(3/4)(3/\pi)^{1/3}\rho^{1/3} \,. \qquad \text{(II-19)}$$

This expression is discussed in Appendix C .

When the system involved has a small number of electrons, N, the exchange energy leads to too much binding. For example, the well-depth for the He_2 interaction as calculated by GK is almost four times greater than that observed experimentally. In view of this, Rae[8](GKR) modified (II-19) by eliminating the contribution due to the self-exchange energy. His formula is

$$\varepsilon_e(GKR;N,\rho) = \gamma(N)\varepsilon_e(GK;\rho), \qquad \text{(II-20)}$$

where

$$\gamma(N) = 1 - 8\delta/3 + 2\delta^2 - \delta^4/3 \,, \qquad \text{(II-21)}$$

and δ is the solution of

$$(4N)^{-1} = \delta^3(1 - 9\delta/8 + \delta^3/4). \qquad \text{(II-22)}$$

This is discussed in the Appendix C .

Rae[16] and Cohen and Pack[9](CP) defined N as the total number of

electrons in the system XY. In subsequent work[8], Rae did a linear extrapolation on $\gamma(N)$ such that

$$\gamma(N) = [\rho_X\gamma(N_X) + \rho_Y\gamma(N_Y)]/\rho_{XY} , \qquad \text{(II-23)}$$

where N_X and N_Y are the number of electrons on atoms (or outer shell) X and Y, respectively. Thus according to Rae, the exchange energy contribution (applied also by (CP)) is

$$V_e(GKR;N,\rho) = \gamma(N)V_e(GK;\rho) . \qquad \text{(II-24)}$$

The difficulties in (II-24) were shown in the application to Argon-CO_2 and Argon-CO potential surfaces by Pack and co-workers.[17] In their work, it was suspected that Rae's correction may overcorrect somewhat. In view of this, an entirely different approach to the exchange energy, which was developed by Handler, is employed in this work.

Handler made a detailed account of the exchange energy as it arises in Thomas-Fermi (TF) theory. He notes that the single particle density matrix is not Hermitian. When he modifies the theory such that a Hermitian matrix is obtained (positive definite), the exchange energy density function is drastically changed from the traditional expression (II-19). (see Appendix D for details)

Handler's formula as given in Reference 10 is not uniformally good. To correct this Handler[18] has subsequently modified his expression, which is given as follows

$$\varepsilon_e(H;N,\rho) = -5.74449\rho^{2/3}/(1 + a\rho^p + b\rho^q + c\rho^r + d\rho^s)^Q \quad \text{(II-25)}$$

where

$$a = 117.15510Z^{-0.46802}$$

$$b = 25.55999Z^{-0.37267}$$

$$c = 42.11950Z^{0.18459}$$

$$d = |11.48898/(0.162748Z^{1.27935})|^{1.5s}$$

$$Q = 2/(3s)$$

$$p = 0.48100Z^{0.10137}$$

(In our case Z = N)

$$q = 0.23273Z^{-0.024536}$$

$$r = 0.44330Z^{0.026373}$$

$$s = 1.072Z^{0.031}$$

and Z is the atomic number. For neutral atoms Z is equal to N. In the proposed calculation, N is taken to be the average number of electrons in the system, $N = (N_X + N_Y)/2$. Consequently, the same value of N is used in each term of the exchange contribution to V_{HF} (II-3). The present estimate, therefore, is

$$V_e(BR;N,R) = \int [\rho_{XY}\varepsilon_e(H;N,\rho_{XY}) - \rho_X\varepsilon_e(H;N,\rho_X) - \rho_Y\varepsilon_e(H;N,\rho_Y)]\, d\vec{r} \,. \quad \text{(II-26)}$$

It may be argued that a more reasonable assumption of N in the first, second and third terms in the above expression should be $N_X + N_Y$, and N_X and N_Y respectively. Difficulties, however, are encountered since the exchange energy from (II-26), using the more "reasonable" assumption for N would be greater than the rest of the terms in (II-3).

To make it clear, a comparison of (II-26) using different N's is made in Table 2. It can be observed that for Ar_2 system, at the equilibrium separation, which is about 7.0 a.u., the exchange energy using different values of N, is three orders of magnitude larger than the kinetic energy contribution. Furthermore, the exchange energy does not tend to go to zero when the internuclear separation R becomes large, i.e., when the atoms are completely separated.

From Fig. 3 an evaluation of the proposed exchange expression (II-26), as applied to Ar_2 system is made in comparison with the standard expression (II-18) and GKR and CP correction (II-24). At small R, CP and the present estimate almost agree, while GKR is relatively more positive. This behavior might have accounted partly for the repulsive potential curve at small R in almost all the systems considered in GKR's calculation. For the intermediate region, the present curve becomes more positive than CP's curve and at large R approaches GKR's curve (Rae's curve). Considering now a system with small number of electrons as in He_2, it is noted (see Fig. 4) that at short and intermediate R, both the GKR's and CP's results overestimates the exchange energy as compared to the present method, and as in previous results, the present curve tends to approach zero faster than the other two at large R.

As the exchange energy is merely a part of the total potential and since the exchange energy for the systems is not definitely known, it can not be decided which approximation; CP or GKR or Handler is the better. However, it should be noted that Handler's expression has a firmer theoretical foundation.

In the light of the above modifications, a thorough evaluation

Table 2. Exchange energy from Handler's expression, using different values for N as applied to Ar_2 ($^1\Sigma_g^+$).[a]

R	GK kinetic energy[b]	$-V_e(H;N,R)$[c]	$-V_e'(H;N,R)$[d]
1.0	0.2080 D 2[e]	0.1322 D 1	0.8030 D 1
1.5	0.1151 D 2	0.8596 D 0	0.7109 D 1
2.0	0.5700 D 1	0.5185 D 0	0.5757 D 1
2.5	0.2713 D 1	0.2971 D 0	0.4601 D 1
3.0	0.1269 D 1	0.1634 D 0	0.3844 D 1
3.5	0.5780 D 0	0.8651 D -1	0.3419 D 1
4.0	0.2566 D 0	0.4440 D -1	0.3202 D 1
4.5	0.1114 D 0	0.2224 D -1	0.3098 D 1
5.0	0.4759 D -1	0.1094 D -1	0.3042 D 1
5.5	0.2007 D -1	0.5297 D -2	0.2998 D 1
6.0	0.8383 D -2	0.2533 D -2	0.2944 D 1
6.5	0.3481 D -2	0.1198 D -2	0.2869 D 1
7.0	0.1442 D -2	0.5621 D -3	0.2770 D 1
7.5	0.5977 D -3	0.2618 D -3	0.2648 D 1
8.0	0.2491 D -3	0.1214 D -3	0.2506 D 1
8.5	0.1048 D -3	0.5617 D -4	0.2349 D 1
9.0	0.4473 D -4	0.2604 D -4	0.2183 D 1
9.5	0.1942 D -4	0.1213 D -4	0.2013 D 1
10.0	0.8600 D -5	0.5702 D -5	0.1844 D 1

[a] All values are in atomic units.

[b] Evaluated from Eqs. (II-11) and (II-12).

[c] Evaluated from Eq. (II-26) with $N = (N_X + N_Y)/2$.

[d] Evaluated from Eq. (II-26) with $N = N_X + N_Y$, $N = N_X$, and $N = N_Y$ for the first, second, and third terms, respectively, in Eq. (II-26).

[e] 0.2080 D 2 is the same as 0.2080×10^2.

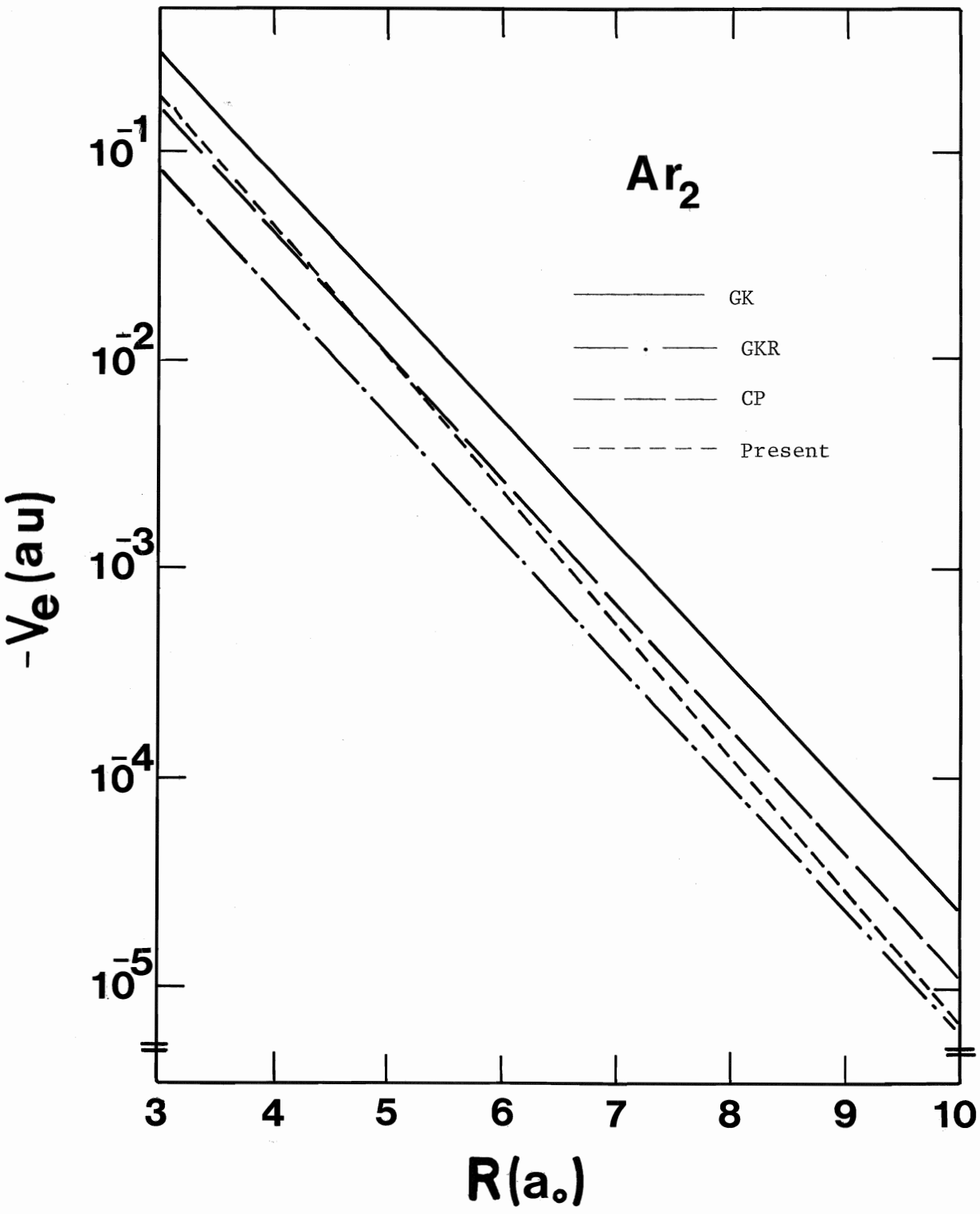

Fig. 3. Exchange energy (V_e) as applied to Ar_2 ($^1\Sigma_g^+$).

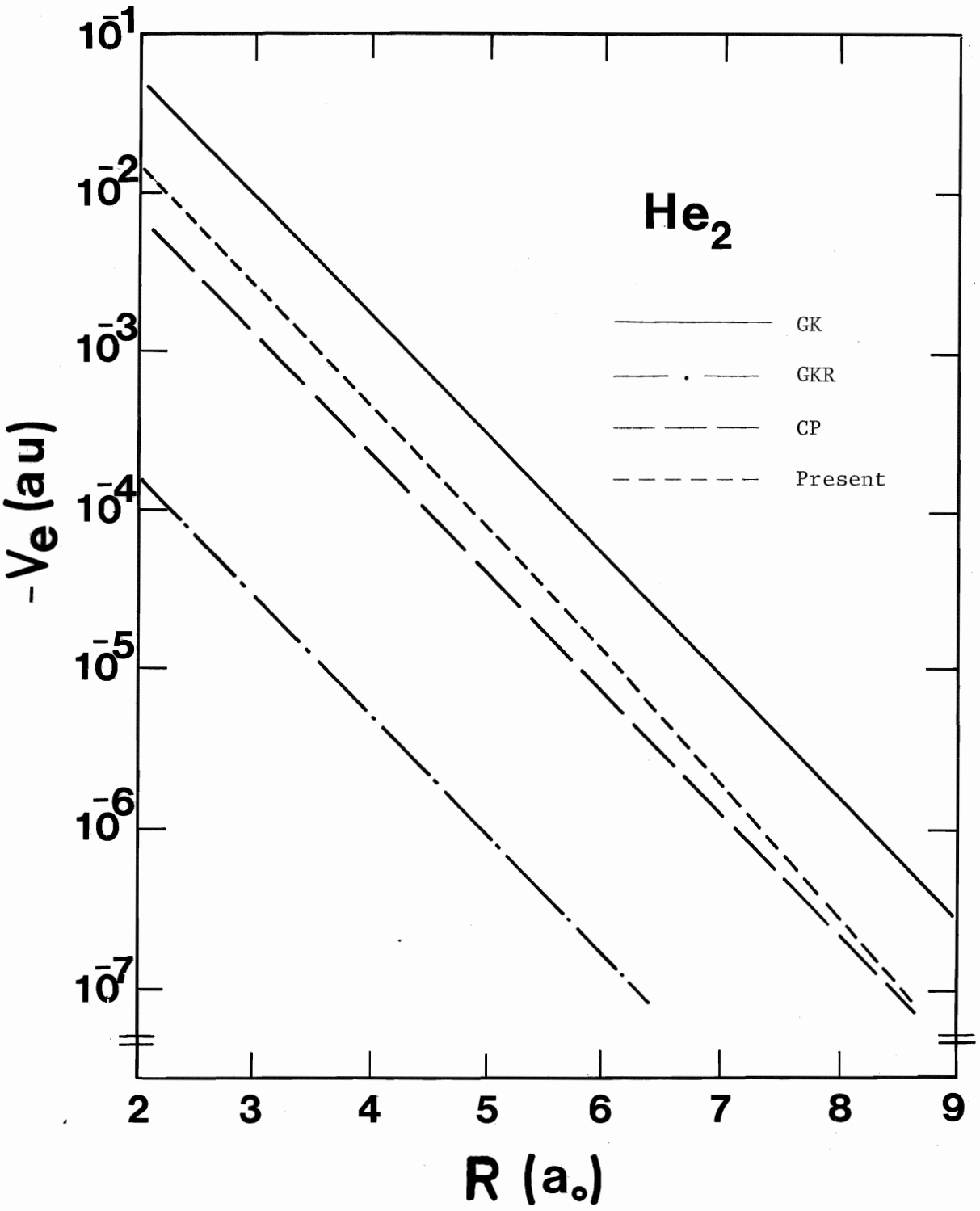

Fig. 4. Exchange energy (V_e) as applied to He_2 ($^1\Sigma_g^+$) .

of the correlation energy expression, with addition of the long-range or dispersive forces, for real systems should be made. This is discussed in detail in the next subsection below.

3. Correlation energy.

The correlation energy used by GK does not make explicit provision for the long-range correlation which is the dispersive energy. Instead, it takes into account the short-range correlation which has the form

$$V_{corr}(GK;R) = \int [\rho_{XY}\varepsilon_{corr}(GK;\rho_{XY}) - \rho_X\varepsilon_{corr}(GK;\rho_X) - \rho_Y\varepsilon_{corr}(GK;\rho_Y)]\, d\vec{r}\,, \qquad \text{(II-27)}$$

where

$$\varepsilon_{corr}(GK;\rho) = 0.0311\ \ell n\ r_s - 0.048 + 0.009\ r_s\ \ell n\ r_s - 0.01\ r_s,$$

$$r_s \leq 0.7 \qquad \text{(II-27a)}$$

$$= -0.06156 + 0.01898\ \ell n\ r_s,\ 0.7 < r_s < 10 \qquad \text{(II-27b)}$$

$$= 0.438\ r_s^{-1} + 1.325\ r_s^{-3/2} - 1.47\ r_s^{-2} - 0.4\ r_s^{-5/2},$$

$$10 \leq r_s \qquad \text{(II-27c)}$$

with $r_s = (3/4\pi\rho)^{1/3}$. Equations (II-27a) and (II-27c) are the high and low density expansions calculated from References 19 and 20 respectively. Equation (II-27b) is a logarithmic interpolation formula made to cover the gap between the regions of the two expansions.

The procedure above warrants further justification. Firstly, the

function is obtainable only in the high and low density limits and one must rely upon an approximate interpolation formula to mimic the behavior of the correlation energy at the most important intermediate densities. Secondly, when the functions are applied to atoms[21], the correlation energy acquired is in poor agreement with those obtained through experiments. For lighter atoms, it overestimates the experimental value by a factor of three and as the number of electrons increases, the factor decreases to a value of about two. For these reasons therefore, the form of the correlation energy can not be employed successfully to real systems. In addition, when the usual correlation energy density expression is used with Handler's exchange correction, poor results are obtained.

Recently, McWeeney[29], in order to bridge the gap between the high and low density expansions, suggested an improved method of calculating the correlation energy. (refer to Appendix E for details) He accurately fits his results over a wide range of densities and comes up with a simple formula,

$$\varepsilon_{corr}(McW;\rho) = -(9.652 + 2.946\rho^{-1/3})^{-1}. \qquad \text{(II-28)}$$

This function is comparable with Wigner's[30] formula applied to actual metallic densities. The above expression (II-28) agrees well with the usual expressions (II-27a) and (II-27c) (see Table 3) and moreover, eliminates interpolation in the intermediate densities.

For the real closed-shell systems like the rare gases, the use of adjustable parameters in (II-28) is immediately suggested, i.e. ,

$$\varepsilon_{corr}^{\alpha,\beta}(BR;\rho) = -(\alpha + \beta\rho^{-1/3})^{-1} \quad . \tag{II-29}$$

The α and β are obtained by adjusting the estimated correlation energy for Helium atom to agree with the accurate value. Thus,

$$V_{corr}^{\alpha,\beta}(BR;\rho_{He}) = \int \varepsilon_{corr}(BR;\rho_{He})\rho_{He}\, d\vec{r} \quad . \tag{II-30}$$

In this way, agreement is ensured with the correlation energy for a prototype (atomic) system. Furthermore, inaccuracies inherent in the uniform electron gas method are minimized. In Table 3, correlation energies for rare gas atoms are reported, as calculated from (II-27), (II-28), and (II-29), after integrating over all space. In comparison with the accepted value, the present work is in the best agreement. Thus, for the diatomic system considered, the contribution of this short-range correlation energy is

$$V_{corr}^{\alpha,\beta}(BR;R) = \int [\rho_{XY}\varepsilon_{corr}^{\alpha,\beta}(BR;\rho_{XY}) - \rho_X\varepsilon_{corr}^{\alpha,\beta}(BR;\rho_X) - \rho_Y\varepsilon_{corr}^{\alpha,\beta}(BR;\rho_Y)]\, d\vec{r} \quad , \tag{II-31}$$

where $\varepsilon_{corr}^{\alpha\ \beta}$ is defined in (II-29) with $\alpha = 9.810$ and $\beta = 21.437$.

At large R, the only interaction energy is the van der Waals (or London) dispersive energy, which depends only on R. Because of the asymptotically divergent nature of this "interatomic" correlation energy, both approaches of GKR and CP include it in some fashion.

CP give the dispersion energy by

$$V_{disp}(CP;R) = -C_6/R^6 - C_8/R^8 - C_{10}/R^{10} \quad , \tag{II-32}$$

Table 3. Correlation energies for rare gas atoms.[a]

Element	GK[b]	McW[c]	This work[d]	Accurate value
He	-0.1165	-0.1286	-0.042045	-0.042045[e]
Ne	-0.7574	-0.7828	-0.3567	-0.381[f]
Ar	-1.457	-1.431	-0.722	-0.732[f]
Kr	-3.334	-3.083	-1.789	

[a] All values are in atomic units and evaluated numerically using a 24-point Gauss Legendre quadrature, following the scheme of McLean and Yoshimine.[13] The wavefunctions are taken from Ref. 11.

[b] Evaluated from (II-27). These results are comparable with those of Ref. 6.

[c] Evaluated from (II-30) but with ε_{corr} from (II-28).

[d] Evaluated from (II-30) and (II-29) with α= 9.810 and β = 21.437. These parameters reproduce an accurate value for the correlation energy for Helium atom.

[e] The exact, non-relativistic energy is taken from C.L. Pekeris, Phys. Rev. 126, 1470 (1962). The Hartree-Fock energy is taken from Ref. 11.

[f] E. Clementi and A. Veillard, J. Chem. Phys. 49, 2415 (1968).

where the C's (van der Waals coefficients) are calculated from the knowledge of the available C_6's and the combining rules. The total correlation energy is then evaluated by

$$V_{corr}(CP;R) = [V_{disp}(CP;R_c)/V_{corr}(GK;R_c)] \times V_{corr}(GK;R) \ ,$$

$$R < R_c \qquad \text{(II-33a)}$$

$$= V_{disp}(CP;R) \ , \quad R \geq R_c \qquad \text{(II-33b)}$$

where R_c is taken as the value of R for which $V_{disp}(CP;R)/V_{corr}(GK;R)$ is a minimum. The above expression is claimed to give a well-behaved, continuous correlation energy function.

In GKR's approach, the dispersive energy is included smoothly at all R by the use of an exponential switching function. His total correlation energy takes the form

$$V_{corr}(GKR;R) = V_{corr}(GK;R) + V_{disp}(GKR;R) \ , \qquad \text{(II-34)}$$

where

$$V_{disp}(GKR;R) = \sum_{n \geq 3}^{n'} f_n \, C_{2n}/R^{2n} \ . \qquad \text{(II-35)}$$

The switching function f_n is given by

$$f_n = 1 \ , \qquad n < n' \qquad \text{(II-36a)}$$

$$f_n^{-1} = \{1 + \exp[-(2R - R_{n'-1,n'} + R_{n',n'+1})/2(R_{n',n'+1} - R_{n'-1,n'})]\} \ , \qquad \text{(II-36b)}$$

where

$$R_{i,j} = (C_{2j}/C_{2i})^{1/2} \quad . \tag{II-37}$$

Finally, for a given R, the value of n' (>3) satisfies

$$R_{n'-1,n} \leq R \leq R_{n',n'+1} \quad . \tag{II-38}$$

As these equations demand that $R \leq R_{3,4}$, the short-range contribution of dispersive energy is not obtained by Rae.

In this paper, as in the approach by Rae (GKR), the total correlation energy is taken as the sum of the short-range and the long-range (dispersive) correlation

$$V_{corr}(BR;R) = V_{corr}^{\alpha,\beta}(BR;R) + V_{disp}(BR;R) \quad . \tag{II-39}$$

where $V_{corr}^{\alpha,\beta}(BR;R)$ is given by (II-31). Because of the divergence of the dispersion expansion, the usual practice of using a fixed number of terms in the series is only good for some limited value of R. Dalgarno and Lewis[23] assert that the error in truncating the series is of the order of magnitude of the smallest term. Therefore, when R increases the number of terms in dispersion series should be increased. The range of R in which n' is smallest is simply calculated by GKR, given in (II-38).

The second term in the right hand side of (II-39) is

$$V_{disp}(BR;R) = \sum_{n\geq 3}^{n'} g_n \, C_{2n}/R^{2n} \quad , \tag{II-40}$$

and g_n can be chosen with range between 0 and 1. As pointed out by Tang and Toennies[24] , the choice of g_n does not have a significant effect on the results since we are dealing with the smallest term. As

with their work, we also choose the simple linear switching function

$$g_n = 1 \quad , \qquad \text{for } n \leq n'-1 \tag{II-41a}$$

$$= (R-R_{n-1,n})/(R_{n,n+1} - R_{n-1,n}) \text{ for } n=n' \tag{II-41b}$$

with $R_{i,j}$ given by (II-37). To prove our point that there is no significant effect on the choice of g_n on the value of V_{disp}, Table 4 is presented. Here, the C's are those used by GKR. It is noted that at small and intermediate R, where V_{disp} has a smaller contribution to the interaction energy, the values in columns two and three agree up to two decimal places. However, at large R, where dispersive energy is the dominating term in the interaction energy, the values agree up to three decimal places.

In the present calculation, the maximum value of n' is 7. Values of the dispersive coefficients used herein are tabulated in Table 5. Since the C_6, C_8 and C_{10} are gotten from the recent work of Tang and co-workers[25] while the C_{12} and C_{14} are crude approximation from Rae, we estimate

$$R_{5,6} = (R_{4,5})^2/R_{3,4} \quad . \tag{II-42}$$

Moreover, $R_{2,3}$ is set to zero and $R_{7,8}$ to $(R_{6,7})^2/R_{5,6}$. The cut-off distances $R_{n,n+1}$ for the terms in the dispersive series are shown in Table 6 .

Table 4. Comparison of the dispersive energy using exponential and linear switching function. Application to Ar_2 ($^1\Sigma_g^+$).[a]

R	$-V_{disp}(GKR;R)$[b]	$-V_{disp}(BR;R)$[c]	C_{2n}[d] and $R_{i,j}$[e]
5.0	0.7533×10^{-2}	0.7598×10^{-2}	$C_6 = 66.89$
5.5	0.5162×10^{-2}	0.5240×10^{-2}	$C_8 = 1176$
6.0	0.2794×10^{-2}	0.2821×10^{-2}	$C_{10} = 29297$
6.5	0.1583×10^{-3}	0.1593×10^{-3}	$C_{12} = 7.559 \times 10^5$
7.0	0.9348×10^{-3}	0.9390×10^{-3}	$C_{14} = 3.353 \times 10^7$
7.5	0.5767×10^{-3}	0.5768×10^{-3}	
8.0	0.3688×10^{-3}	0.3685×10^{-3}	$R_{3,4} = 4.19$
8.5	0.2434×10^{-3}	0.2436×10^{-3}	$R_{4,5} = 5.00$
9.0	0.1656×10^{-3}	0.1657×10^{-3}	$R_{5,6} = 5.08$
9.5	0.1156×10^{-3}	0.1157×10^{-3}	$R_{6,7} = 6.66$
10.0	0.8265×10^{-3}	0.8267×10^{-3}	$R_{7,8} = 8.73$

[a] All values are reported in atomic units.

[b] Reported in Table 2 of Ref. 8

[c] Evaluated from (II-40) and (II-41).

[d] Obtained from Ref. 8.

[e] Evaluated from (II-37).

Table 5. Van der Waals coefficients for the rare gas diatomics.[a]

System	C_6[b]	C_8[b]	C_{10}[b]	C_{12}[c]	C_{14}[c]
He-He	1.42	14.2	169.8	3535	88842
Ne-Ne	6.87	76.0	1100	13166	3.278×10^5
Ar-Ar	67.2	1480	42700	7.559×10^5	3.353×10^7
Kr-Kr	133	3180	89800	2.15×10^6	9.631×10^7
He-Ne	3.13	32.7	429	6592	1.646×10^5
He-Ar	9.82	153.5	3247	59889	2.256×10^6
He-Kr	13.6	226.4	4598	1.051×10^5	3.871×10^6
Ne-Ar	20.7	344	7730	1.151×10^5	4.339×10^6
Ne-Kr	28.7	504	10910	2.018×10^5	7.379×10^6
Ar-Kr	94.3	2170	61700	1.278×10^6	5.663×10^7

[a] All values are in atomic units.

[b] From Ref. 25.

[c] Evaluated by Rae using the formula derived by G. Starkschall and R.G. Gordon, J. Chem. Phys. 54, 663 (1971).

Table 6. Calculated cut-off distances for the various terms in the dispersion series.[a]

System	$R_{3,4}$	$R_{4,5}$	$R_{5,6}$[b]	$R_{6,7}$	$R_{7,8}$[c]
He-He	3.11	3.46	3.85	5.01	6.53
Ne-Ne	3.33	3.80	4.35	5.00	5.72
Ar-Ar	4.69	5.37	6.15	6.66	7.22
Kr-Kr	4.89	5.31	5.78	6.69	7.76
He-Ne	3.23	3.62	4.06	5.00	6.15
He-Ar	3.95	4.60	5.35	6.14	7.04
He-Kr	4.08	4.51	4.98	6.07	7.40
Ne-Ar	4.08	4.74	5.51	6.14	6.84
Ne-Kr	4.19	4.65	5.17	6.05	7.08
Ar-Kr	4.80	5.33	5.93	6.66	7.48

[a] All values are reported in atomic units. The dispersion coefficients used are those tabulated in Table 5. Except for $R_{5,6}$ and $R_{7,8}$ all are calculated from (II-37).

[b] Estimated by assuming $R_{5,6}/R_{4,5} \simeq R_{4,5}/R_{3,4}$.

[c] Estimated by assuming $R_{7,8}/R_{6,7} \simeq R_{6,7}/R_{5,6}$.

4. Summary.

In summary, the interatomic interaction energy used in this work is the sum of Equations (II-11),(II-26), and (II-39), which are the kinetic, exchange and correlation energy contributions respectively. Except for the dispersive energy, which can be calculated directly with the knowledge of the van der Waals coefficients, the integrals are conveniently evaluated by the use of a spheroidal coordinate system.

A 24-point Gauss-Legendre quadrature is used for the angular variable (η) and a 24-point Gauss-Laguerre quadrature is employed for the radial variable (ξ).

The subtraction of the atomic contributions in the integrand of (II-11), (II-26) and (II-31) is important in attaining numerically significant results. If we instead separate the atomic contributions, which are constant at all R, it would be necessary to calculate them to more than ten significant figures[6]. Certainly, this is a prohibitive task in regard to the convergence of the integrals using the quadrature scheme and in regard to economy on computer time.

Thus, from the Coulombic (II-6), and the interatomic interaction energy, the total interaction could be calculated.

Applications of the present approach are presented in subsequent chapters.

C H A P T E R III

APPLICATION TO RARE GAS INTERACTIONS.

Using the procedure discussed in the previous chapter, the interaction potentials (IMF) have been calculated for a number of closed-shell atoms. The results are presented in Table 7, and comparison with the calculated potentials by Rae (GKR) and Cohen and Pack (CP) and with the experimental findings is shown in Figs. 5-14.

For homonuclear systems, X_2, the agreement between the theory and experiment is excellent in contrast with the results of GKR where the potential wells become too shallow for larger diatoms, and with the results of CP, where the wells are too shallow for small systems. In the region of small separation, i.e., $R_m/2 < R < \sigma$ (σ is the point where the potential curve crosses the abscissa), GKR's result are too repulsive in all cases, while the present and CP's curves, except for He_2, are in good accord with the experiment.

For heteronuclear systems, XY , the agreement between theory and experiment is satisfactory, although not as good as that for the homonuclear cases. For the He-X potentials, the statistical theories yield potentials that are deep in the minimum, and those for Ne-X are shallow. However, it should be noted that there are considerable discrepancies among the experimental potentials reported for these systems. For example, different experimental works give He-Ne well depths that are off by almost a factor of two.[26] In the recent paper of Tang and Toennies[24] the results of Buck et. al.[27], R_m (3.01 Å) and ϵ (1.89 meV) for He-Ne

are quoted, which essentially agree within the experimental error, with the present calculated results. The work of Buck and co-workers is the most recent result for He-Ne, and it is in good agreement with the earlier findings of Haningen et al.[27] Other papers on the He-Ne are those published by Chen et al[26] which are displayed in Fig. 9, and by Pirani and Vecchiocattivi[37]. For the He-Ar and He-Kr systems (Figs. 10 and 11 respectively), the results of Chen et al are shown. Recent works[37,38] however, have deeper well depths. The comparisons are clearly depicted in Table 8. For Ar-Kr, our result agrees with three independent and consistent experimental findings[28-31] better than the other competing statistical calculations.

For He-X systems, comparing the three models, the same trend could be observed as in the homonuclear cases, i. e., for the small system like He-Ne, the potential well by CP is the shallowest, while for the large system like He-Kr GKR's curve is the shallowest.

In all cases there is a good agreement in the long-range region ($R \geq R_m + 2$) where the only interaction energy is that due to dispersion. This is clearly seen in Fig. 15. Here, it is evident that all other contributions to the total potential at large R are negligible compared to dispersive effects, and therefore the accuracy of the potential curve in this region would be dependent on the accuracy of the van der Waals coefficients .

Overall a very significant result is that we reproduce accurately the He-He potential, the very system which one would expect failure due to the statistical nature of the theory. Furthermore, an important

link between the short- and long-range theories has been established by parameterizing the short-range correlation energy density function (II-29) to agree with the accurate correlation energy for the Helium atom and by including the dispersive energy at all R which is appropriately truncated and smoothly added by the use of a simple switching function (II-41).

Table 7. Rare gas interaction potential energies. At the bottom the calcu lated properties are compared with experimental values (in parentheses).[a]

	V(R)									
R (a_o)	He-He	Ne-Ne	Ar-Ar	Kr-Kr	He-Ne	He-Ar	He-Kr	Ne-Ar	Ne-Kr	Ar-Kr
2.0	0.1190 D 0									
2.5	0.3774 D -1[b]									
3.0	0.1284 D -1	0.1104 D 0	0.4679 D 0	0.8772 D 0	0.3573 D -1	0.1062 D 0	0.1284 D 0	0.2967 D 0	0.3997 D 0	0.6214 D 0
3.5	0.3490 D -2	0.3280 D -1	0.2245 D 0	0.3999 D 0	0.1032 D -1	0.3875 D -1	0.5523 D -1	0.1172 D 0	0.1684 D 0	0.2945 D 0
4.0	0.8720 D -3	0.8617 D -2	0.1030 D 0	0.1882 D 0	0.2472 D -2	0.1462 D -1	0.2268 D -1	0.4413 D -1	0.6824 D -1	0.1390 D 0
4.5	0.1846 D -3	0.2038 D -2	0.4537 D -1	0.9061 D -1	0.5627 D -3	0.4658 D -2	0.7733 D -2	0.1489 D -1	0.2511 D -1	0.6392 D -1
5.0	0.6654 D -6	0.3243 D -3	0.1698 D -1	0.3892 D -1	0.4660 D -4	0.1253 D -2	0.2329 D -2	0.4396 D -2	0.8189 D -2	0.2575 D -1
5.5	-0.3417 D -4	-0.7889 D -4	0.4868 D -2	0.1116 D -1	-0.6169 D -4	0.1839 D -3	0.5897 D -3	0.9316 D -3	0.2282 D -2	0.7912 D -2
6.0	-0.3106 D -4	-0.1216 D -3	0.1037 D -2	0.3874 D -2	-0.6412 D -4	-0.6893 D -4	0.7360 D -4	0.5441 D -4	0.5932 D -3	0.2043 D -2
6.5	-0.2244 D -4	-0.9988 D -4	-0.2599 D -3	0.5383 D -3	-0.4776 D -4	-0.1145 D -3	-0.9218 D -4	-0.1808 D -3	-0.4863 D -4	0.6109 D -4
7.0	-0.1502 D -4	-0.975 D -4	-0.4740 D -3	-0.2927 D -3	-0.3234 D -4	-0.9458 D -4	-0.1052 D -3	-0.1764 D -3	-0.1626 D -3	-0.4477 D -3
7.5	-0.9967 D -5	-0.4726 D -4	-0.4383 D -3	-0.6093 D -3	-0.2153 D -4	-0.6917 D -4	-0.8910 D -4	-0.1401 D -3	-0.1696 D -3	-0.5214 D -3
8.0	-0.6672 D -5	-0.3182 D -4	-0.3252 D -3	-0.5337 D -3	-0.1441 D -4	-0.4762 D -4	-0.6470 D -4	-0.9833 D -4	-0.1294 D -3	-0.4235 D -3
8.5	-0.4552 D -5	-0.2174 D -4	-0.2372 D -3	-0.4300 D -3	-0.9822 D -5	-0.3303 D -4	-0.4605 D -4	-0.6943 D -4	-0.9522 D -4	-0.3216 D -3
9.0	-0.3181 D -5	-0.1513 D -4	-0.1693 D -3	-0.3253 D -3	-0.6834 D -5	-0.2305 D -4	-0.3250 D -4	-0.4880 D -4	-0.6832 D -4	-0.2353 D -3
9.5	-0.2256 D -5	-0.1074 D -4	-0.1202 D -4	-0.2387 D -3	-0.4855 D -5	-0.1630 D -4	-0.2304 D -4	-0.3454 D -4	-0.4875 D -4	-0.1700 D -3
10.0	-0.1636 D -5	-0.7775 D -5	-0.8680 D -4	-0.1746 D -3	-0.3516 D -5	-0.1176 D -4	-0.1658 D -4	-0.2499 D -4	-0.3521 D -4	-0.1231 D -3
R_m (a_o)	5.64	5.98	7.12	7.56	5.77	6.47	7.02	6.73	7.27	7.40
	(5.60)[32]	(5.88)[33]	(7.11)[34]	(7.57)[35]	(5.69)[27]	(6.54)[38]	(6.94)[38]	(6.48)[36]	(6.77)[36]	(7.33)[31]
ϵ (a.u.)	-0.351 D -4	-0.124 D -3	-0.485 D -3	-0.609 D -3	-0.691 D -4	-0.117 D -3	-0.106 D -3	-0.190 D -3	-0.177 D -3	-0.530 D -3
	(-0.349 D -4)[32]	(-0.135 D -3)[33]	(-0.450 D -3)[34]	(-0.629 D -3)[35]	(-0.695 D -4)[27]	(-0.956 D -4)[38]	(-0.956 D -4)[38]	(-0.228 D -3)[36]	(-0.236 D -3)[36]	(-0.546 D -3)[31]
σ (a.u.)	5.0	5.3	6.4	6.9	5.2	5.8	6.2	6.0	6.4	6.7
	(4.97)[32]	(5.23)[33]	(6.32)[34]	(6.87)[35]	(5.16)[27]	(5.84)[38]	(6.20)[38]	(5.84)[36]	(6.09)[36]	(6.70)[31]

[a] All values are in atomic units.

[b] 0.3774 D -1 is the same as 0.3774×10^{-1}.

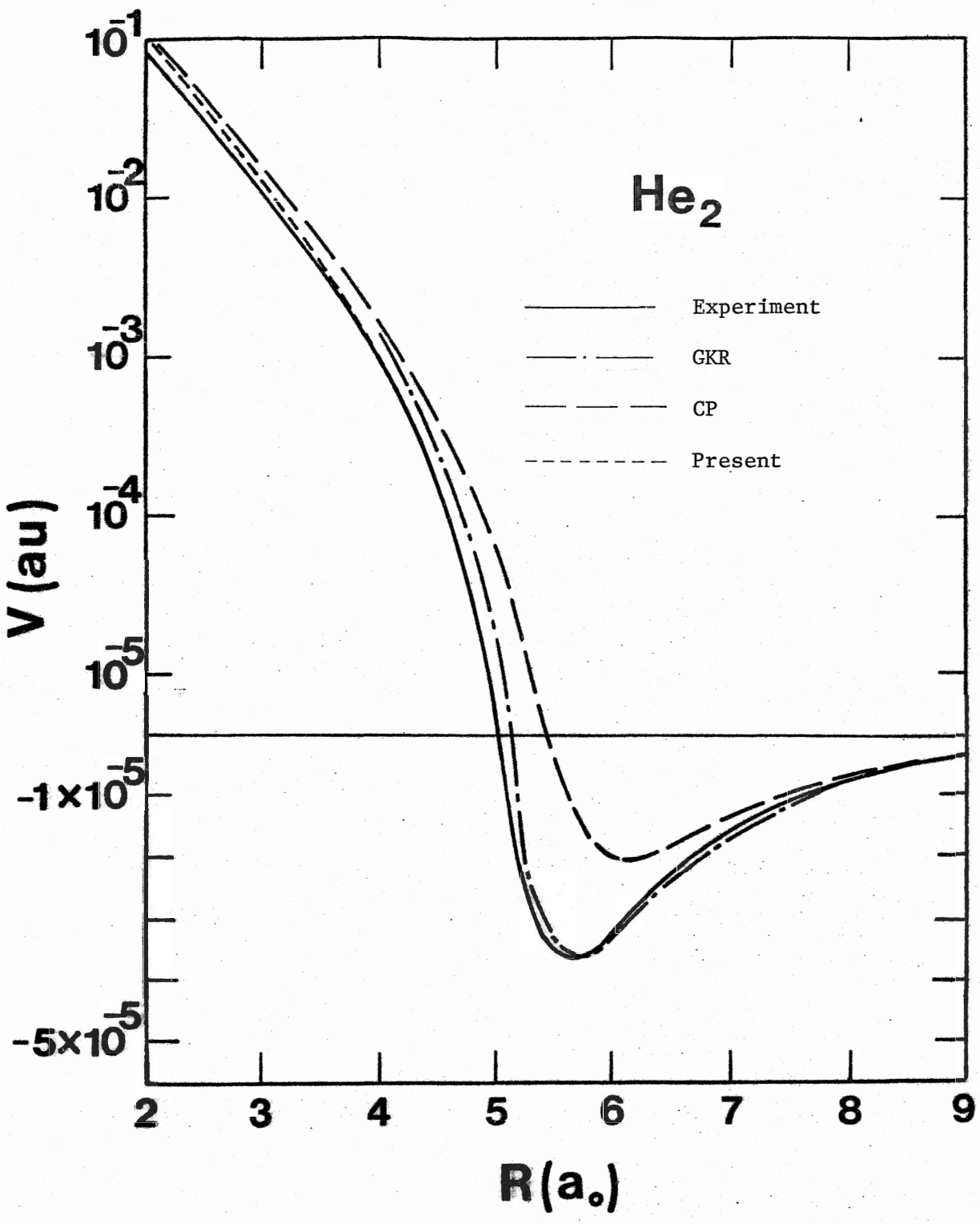

Fig. 5. Comparison of the interaction energy for He_2 ($^1\Sigma_g^+$). The experimental curve is taken from Ref. 32.

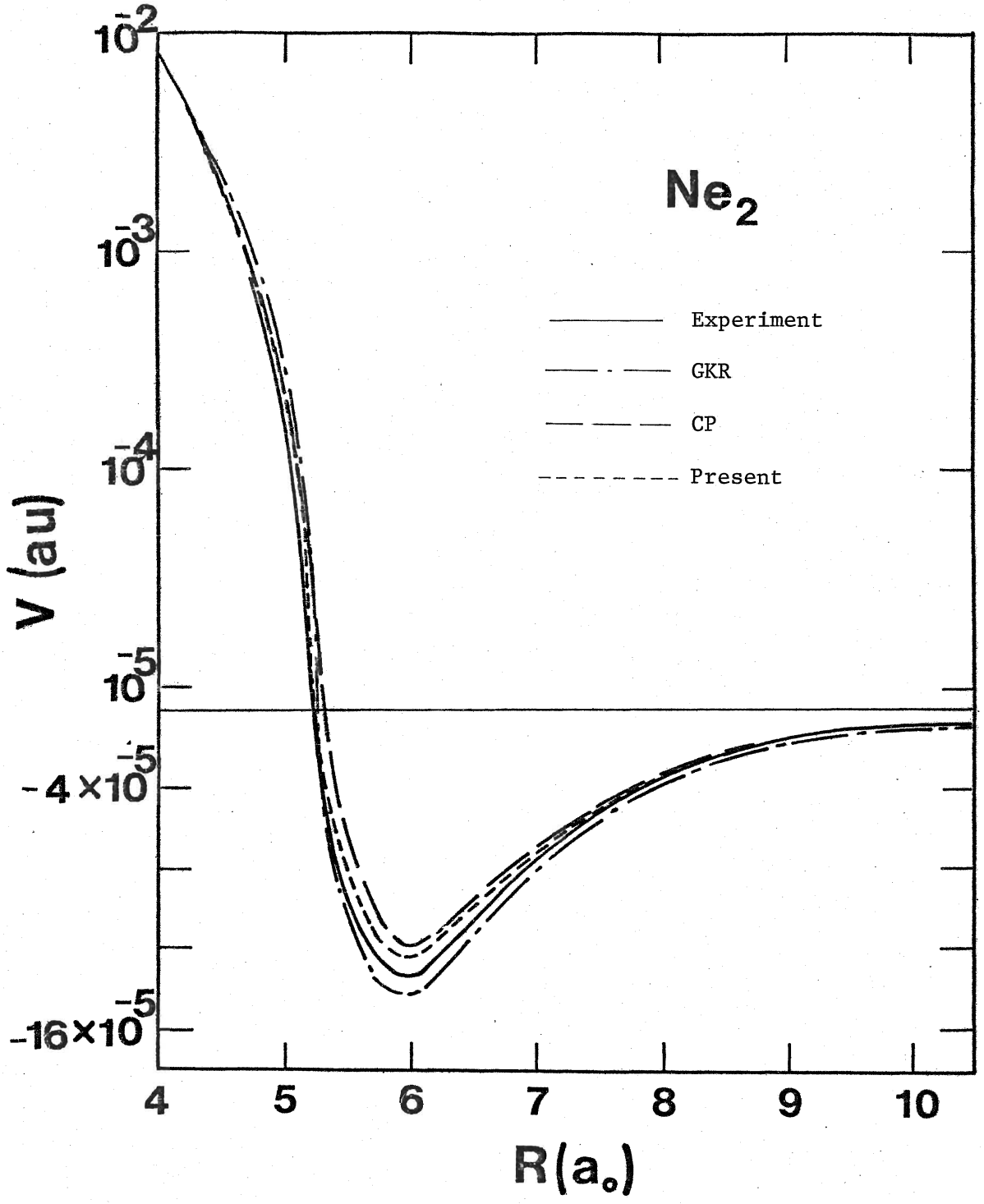

Fig. 6. Comparison of the interaction energy for Ne_2 ($^1\Sigma_g^+$). The experimental curve is taken from Ref. 33.

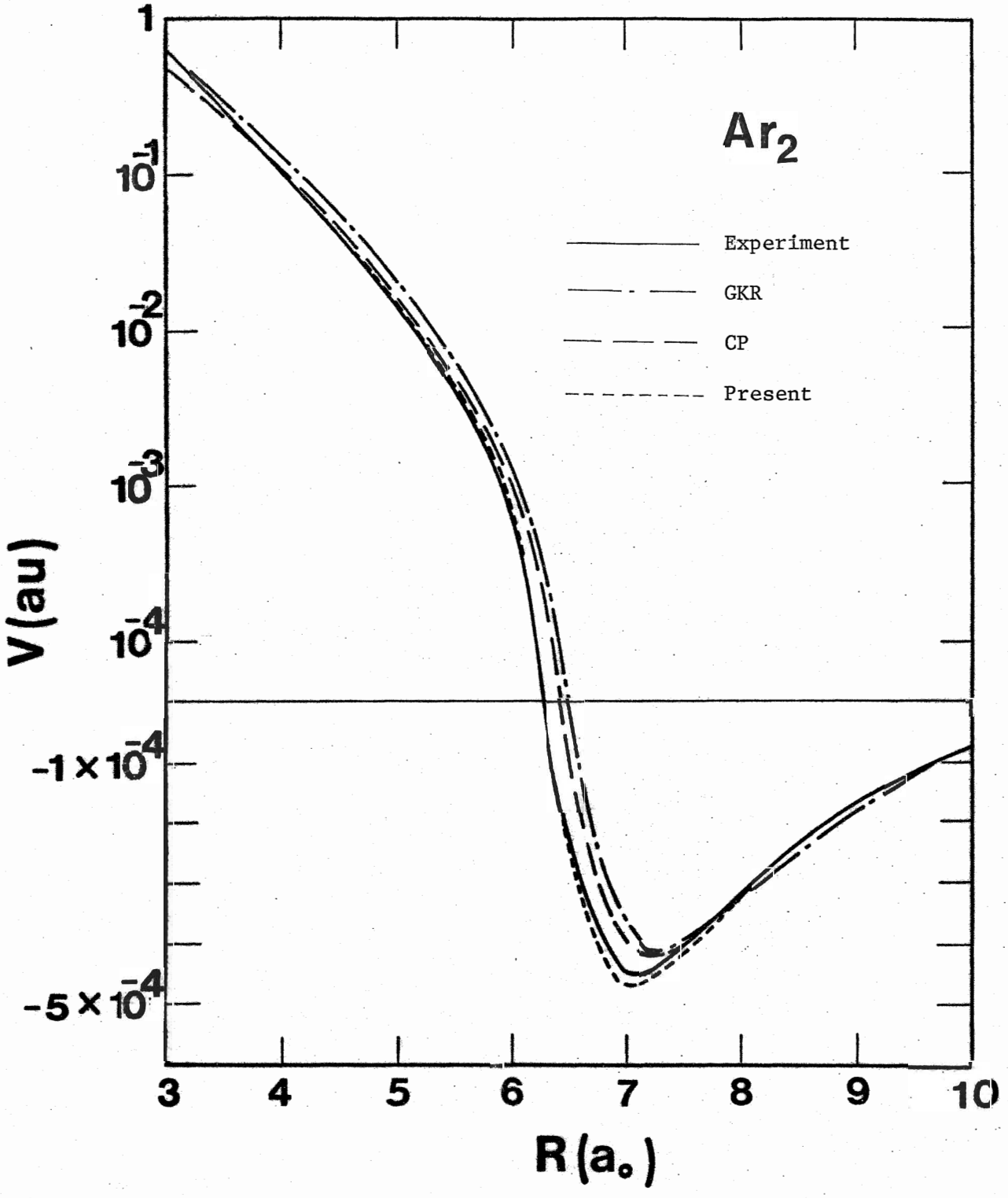

Fig. 7. Comparison of the interaction energy for Ar_2 ($^1\Sigma_g^+$). The experimental curve is taken from Ref. 34.

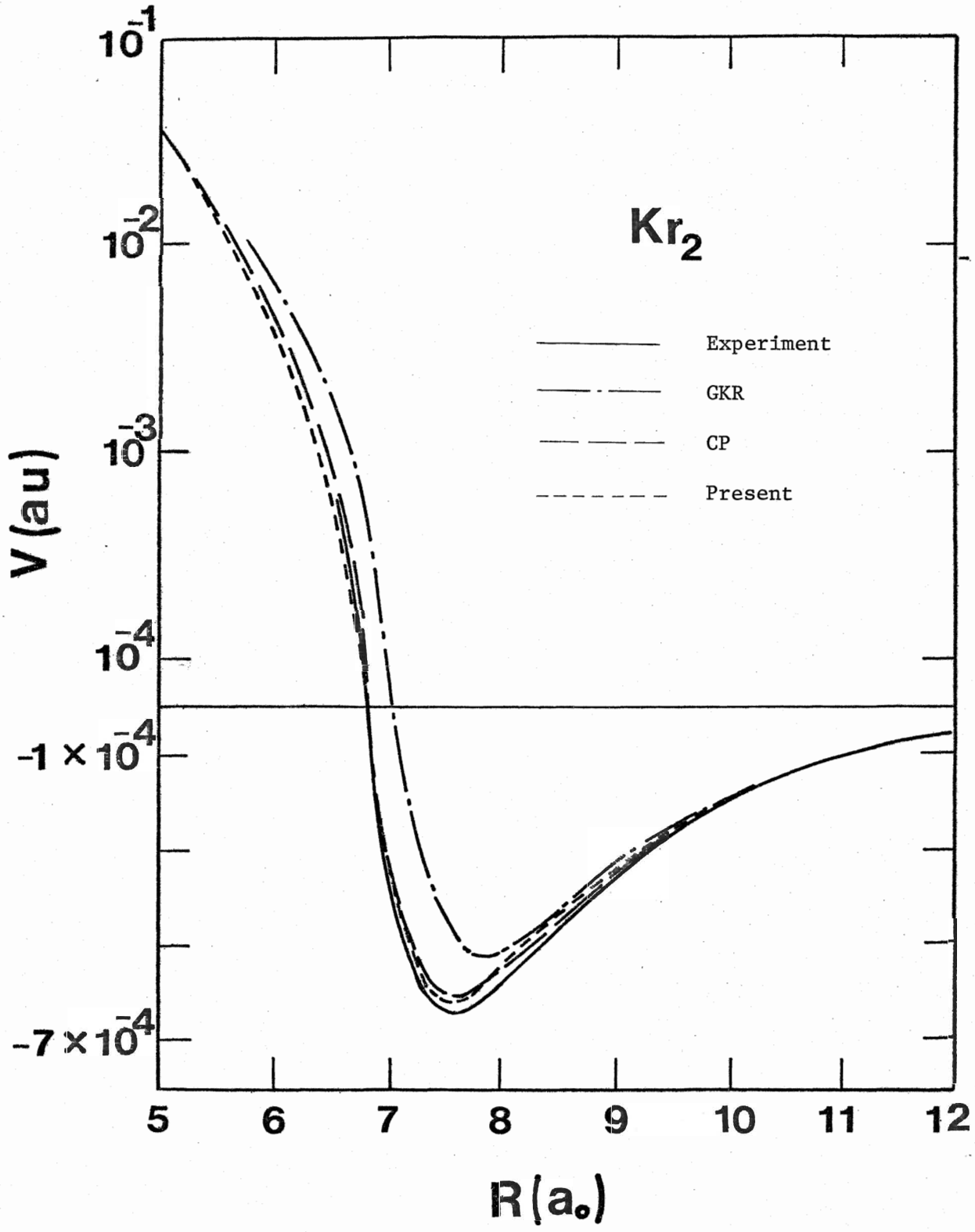

Fig. 8. Comparison of the interaction energy for Kr_2 ($^1\Sigma_g^+$). The experimental curve is taken from Ref. 35.

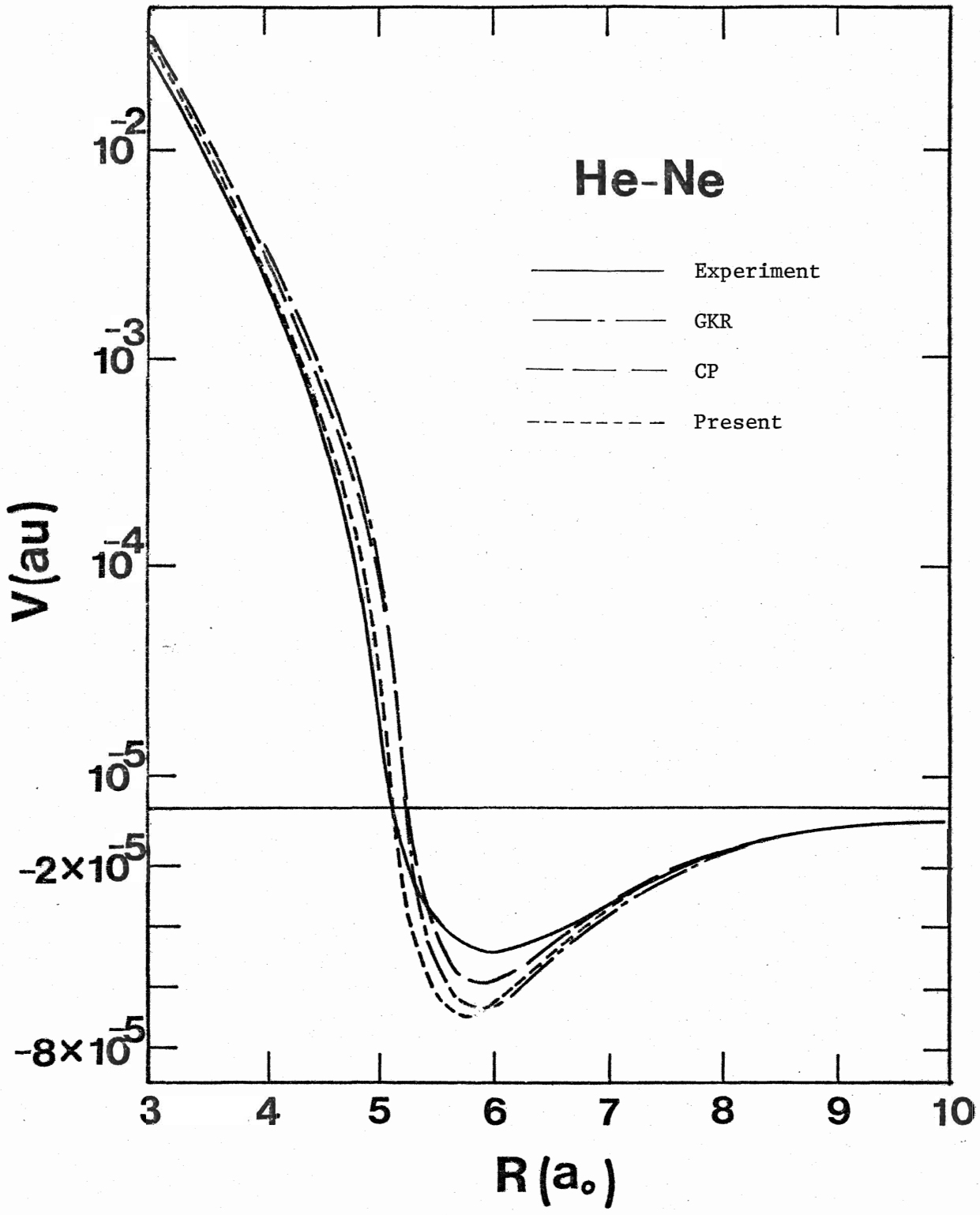

Fig. 9. Comparison of the interaction energy for He-Ne ($^1\Sigma^+$). The experimental curve is taken from Ref. 26.

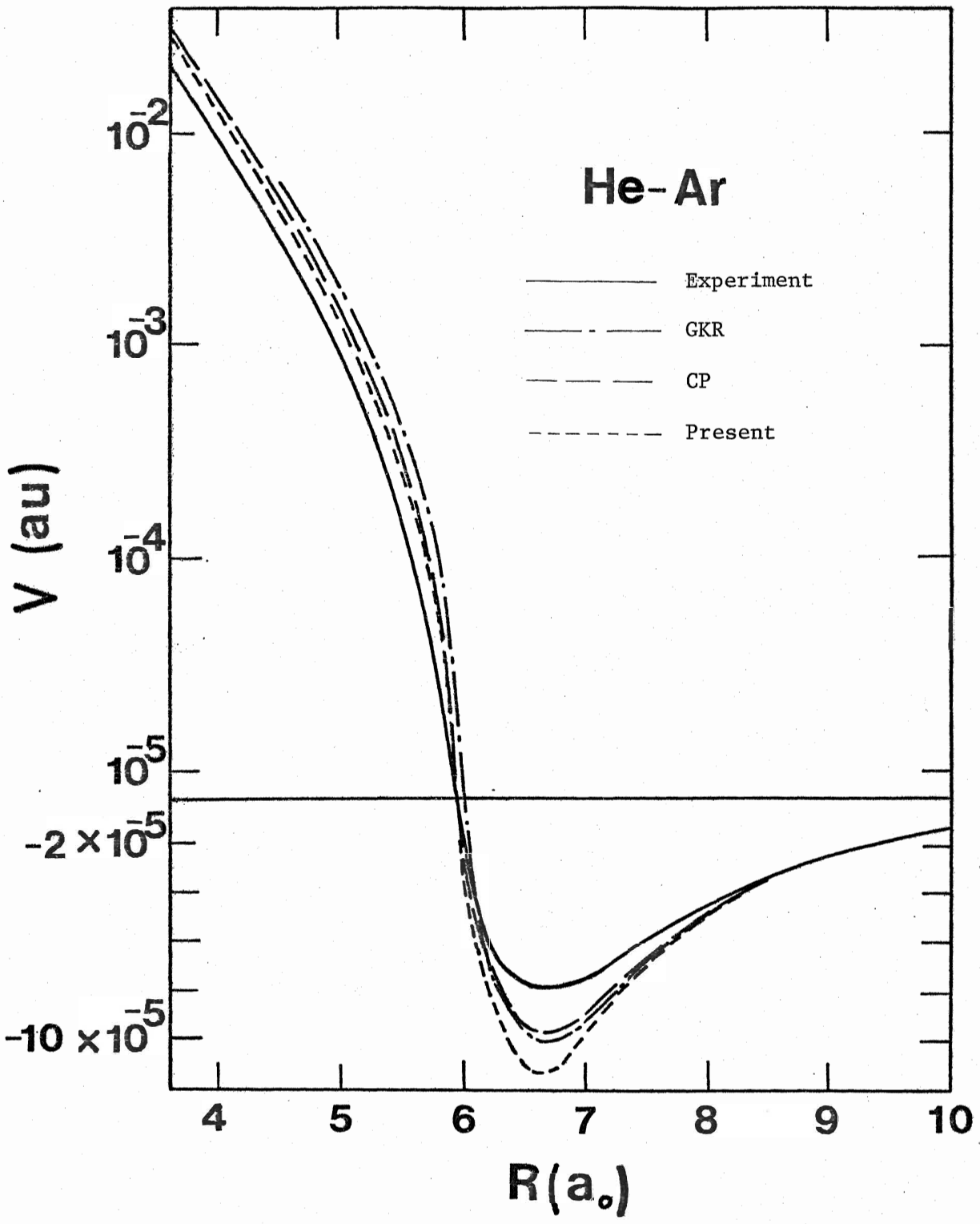

Fig. 10. Comparison of the interaction energy for He-Ar ($^1\Sigma^+$). The experimental curve is taken from Ref. 26.

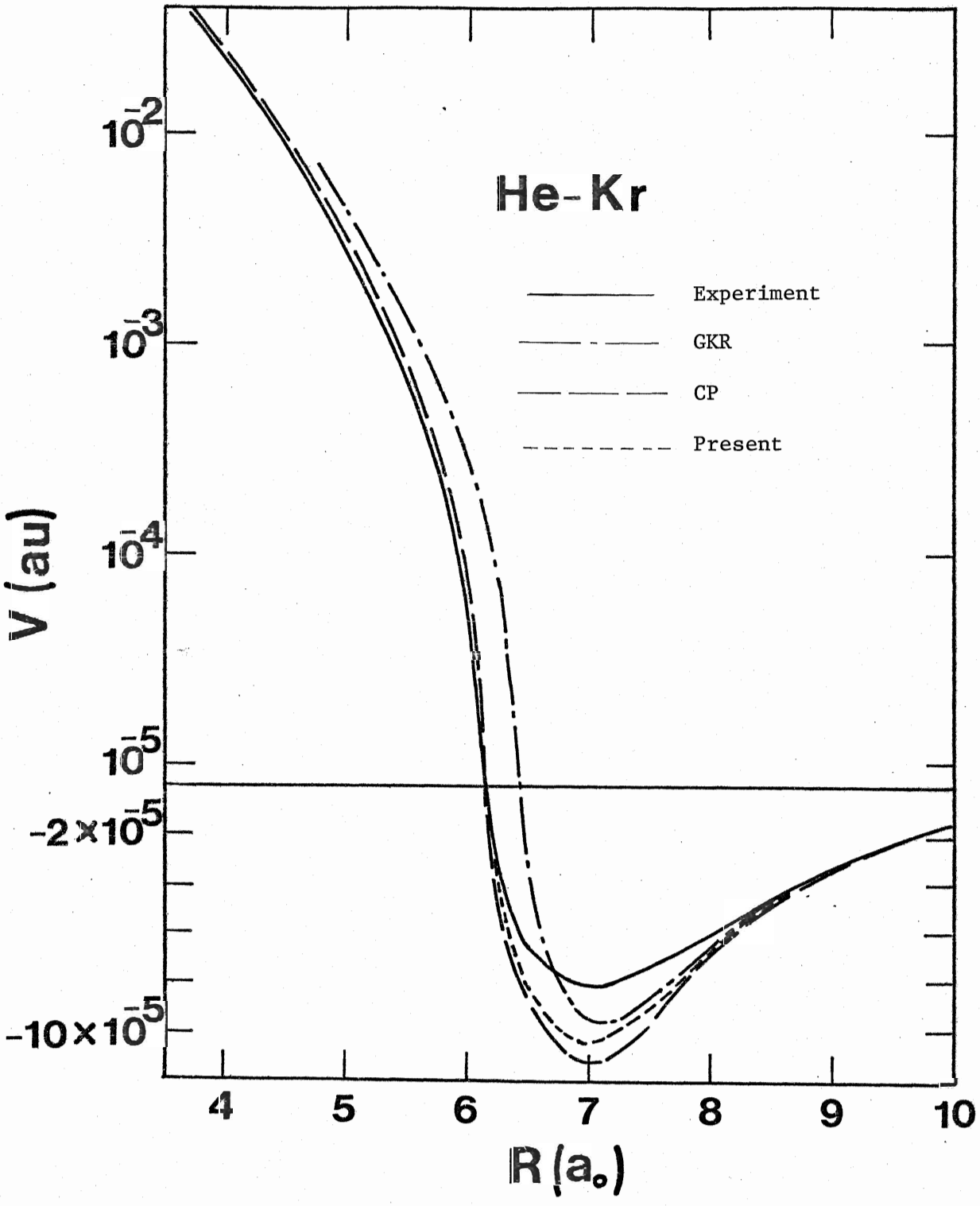

Fig. 11. Comparison of the interaction energy for He-Kr ($^1\Sigma^+$). The experimental curve is taken from Ref. 26.

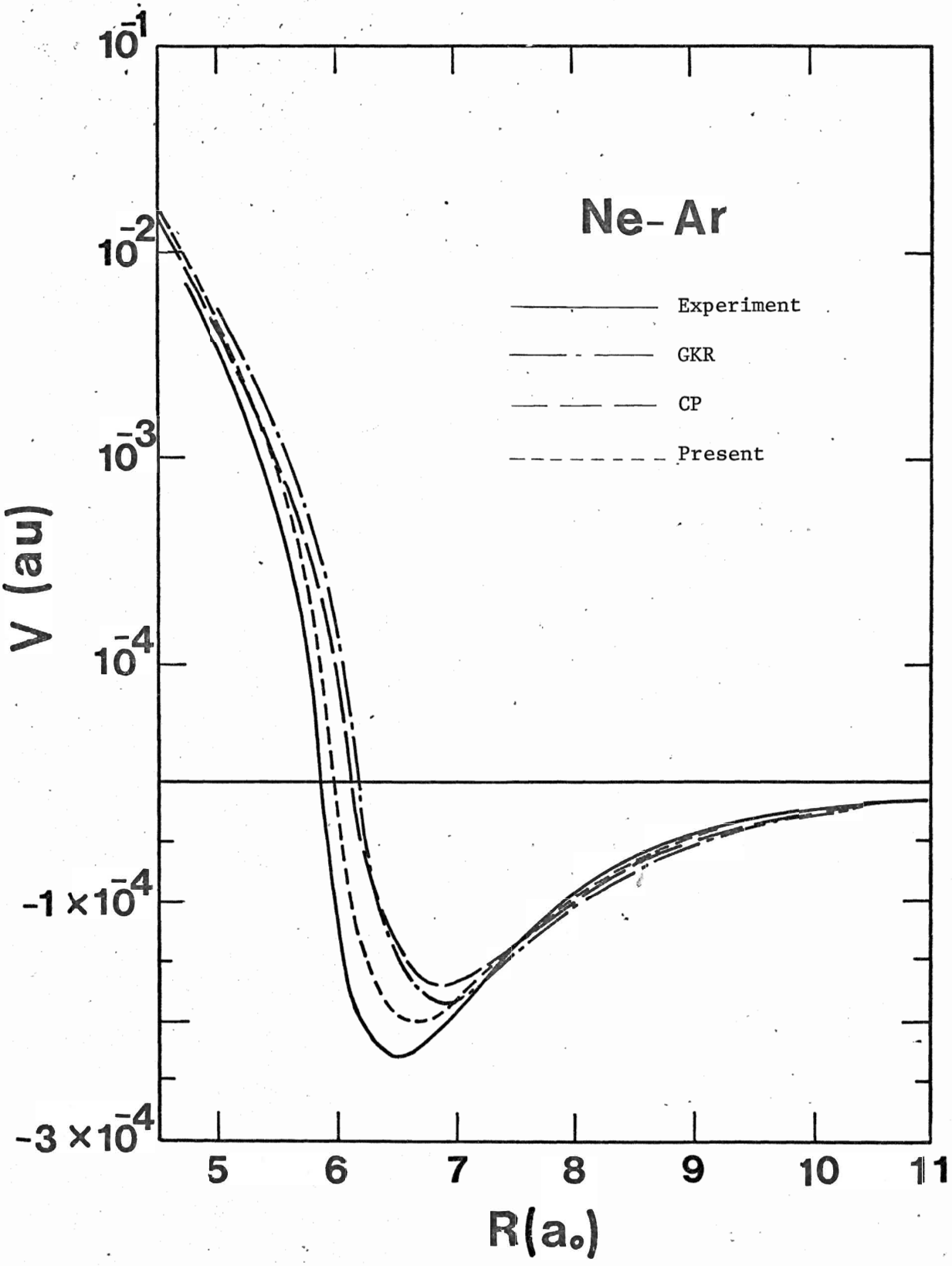

Fig. 12. Comparison of the interaction energy for Ne-Ar ($^1\Sigma^+$). The experimental curve is taken from Ref. 36.

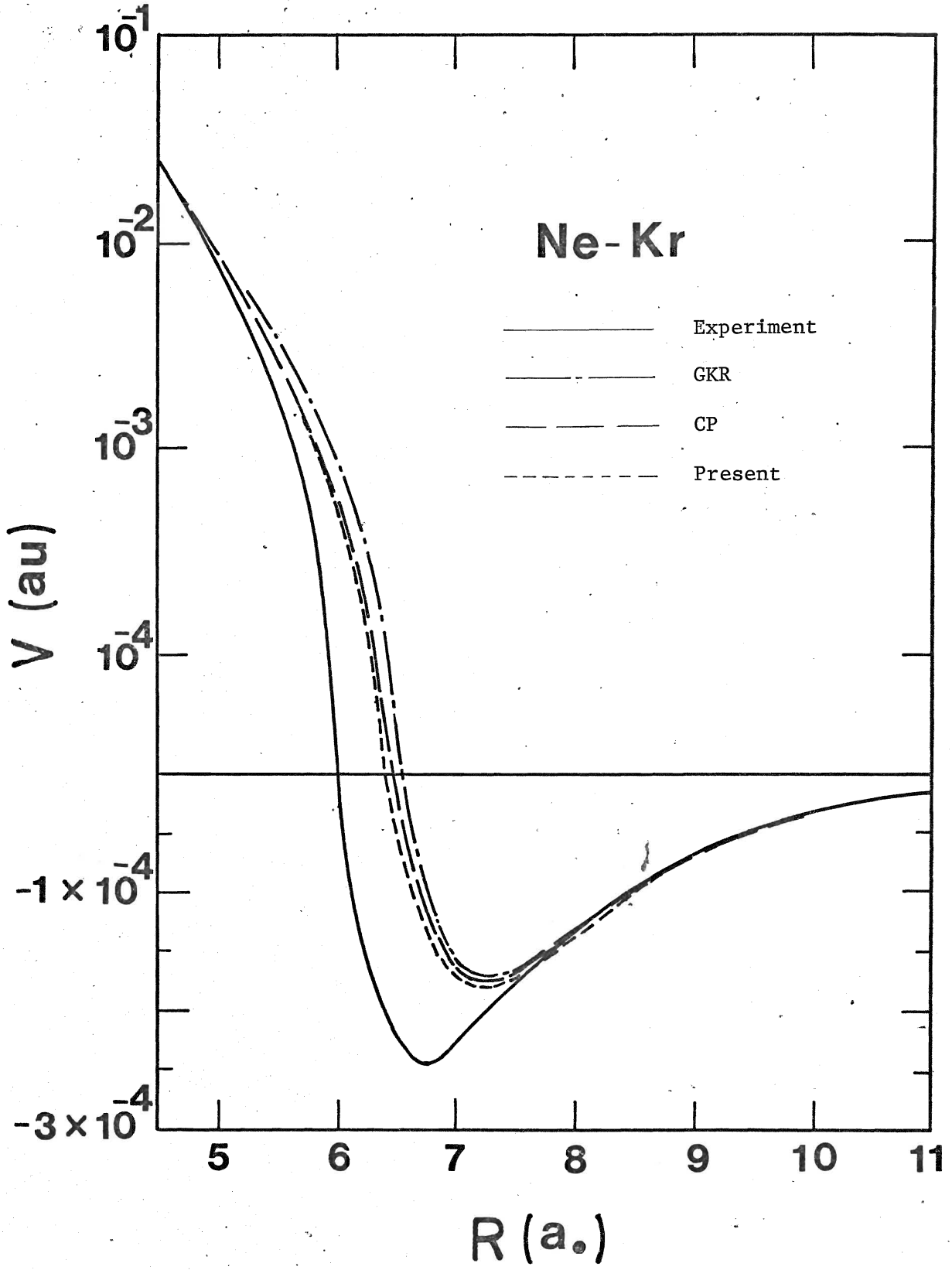

Fig. 13. Comparison of the interaction energy for Ne-Kr ($^1\Sigma^+$). The experimental curve is taken from Ref. 36.

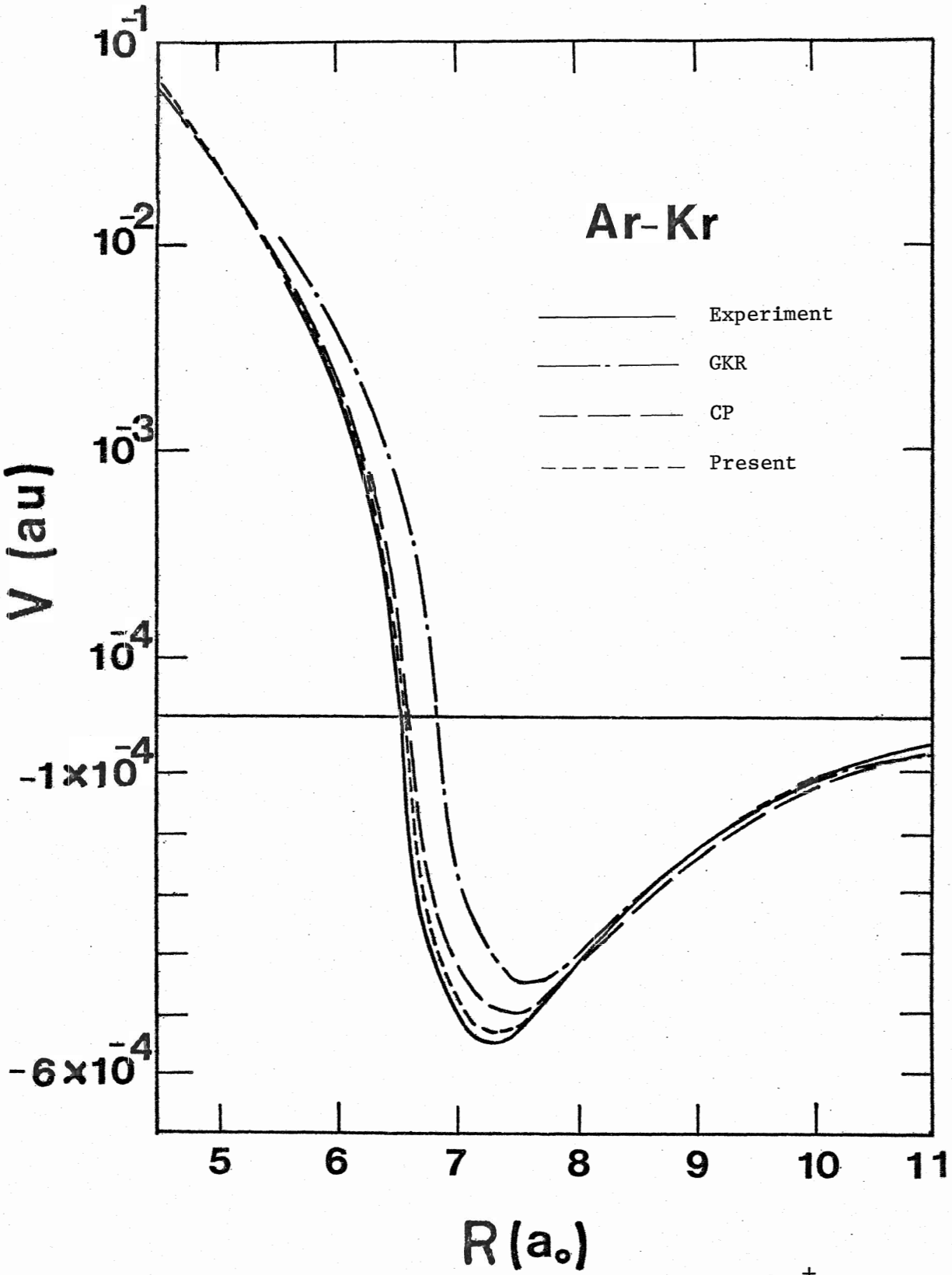

Fig. 14. Comparison of the interaction energy for Ar-Kr ($^1\Sigma^+$). The experimental curve is taken from Ref. 28.

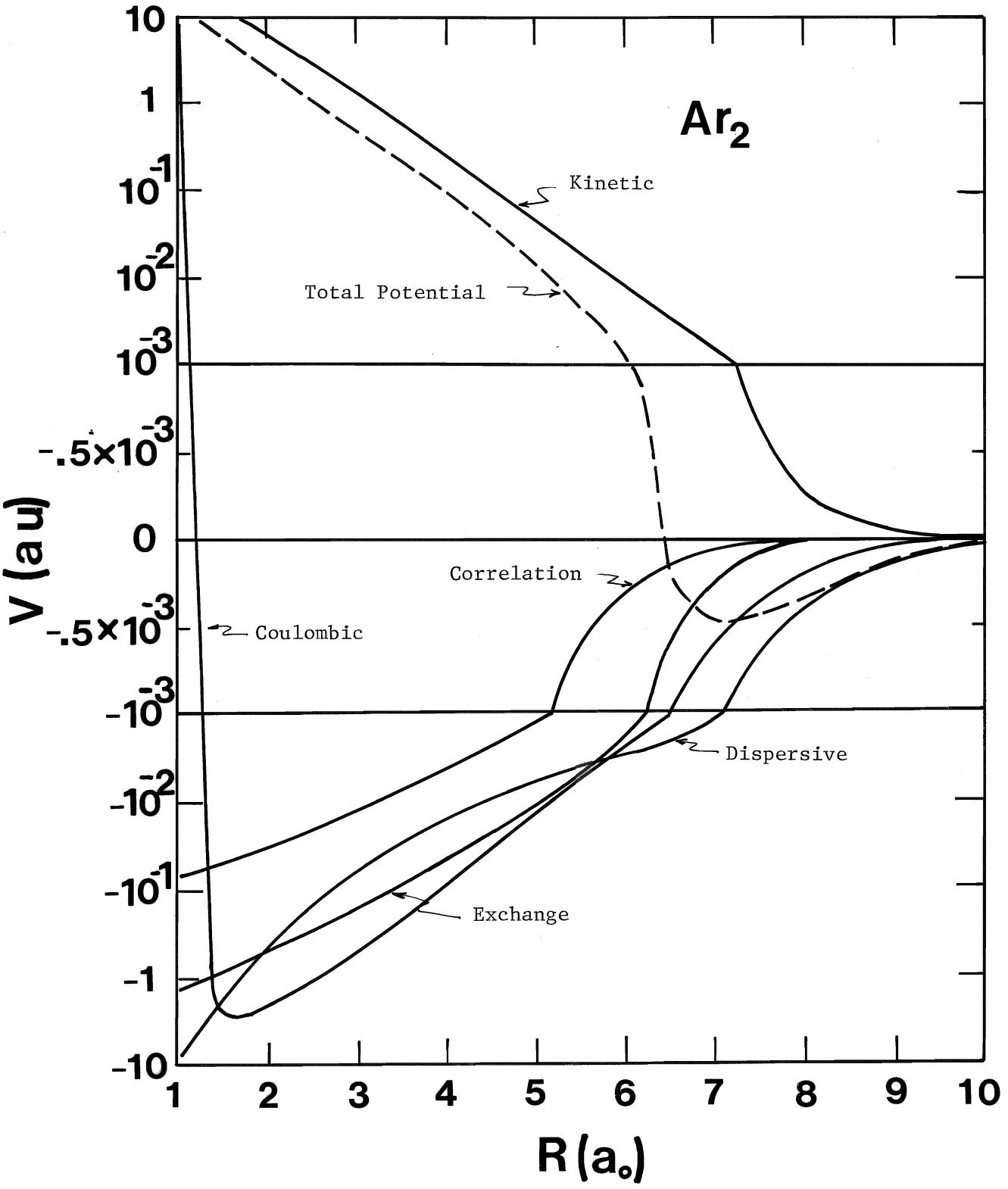

Fig. 15. Individual terms in Ar-Ar IMF potential.

Table 8. Potential parameters for He-rare gas interactions[a]

System	ϵ ($\times 10^5$)	R_m	σ	Reference
He-Ne	6.91	5.77	5.16	This work
	4.53±0.13	6.07	--	26
	6.95	5.69	5.16	27
	5.42	6.14±0.06	5.16	34
He-Ar	11.7	6.47	5.84	This work
	7.66±0.54	6.69±0.02	5.84	26
	8.52±0.20	6.71±0.06	5.84	37
	9.56±0.80	6.54±0.06	5.84±0.06	38
He-Kr	10.6	7.02	6.17	This work
	7.82±0.44	7.09±0.06	6.17	26
	8.55±0.20	7.12±0.08	6.17	37
	9.56±0.80	6.94±0.06	6.20±0.06	38

[a] All values are in atomic units.

C H A P T E R IV

APPLICATION TO HYDROGEN ATOM - RARE GAS INTERACTIONS.

The possibility of applying the statistical method in the interaction of Hydrogen atom (open-shell) with a noble gas (closed-shell) is studied in this chapter. The method is useful in these systems because they do not form strong chemical bonds, unlike the case for the interaction of two open-shell atoms. Thus, the distortion of the electron distribution as the atoms are brought together is expected to be minimal, rendering the main assumption, additivity of atomic densities, valid.

Employing the exact density for hydrogen atom, $\rho = e^{-2r}/\pi$, and the available C_6, C_8 and C_{10}[25] for He-H, Ne-H, Ar-H and Kr-H, the potential curves for these systems are constructed from the present statistical theory, and the results are compared to recent theoretical and/or experimental works available. (see Figs. 16-19)

The He-H system, a simple three-electron diatom, has been the subject of numerous theoretical studies[41,43,44,45]. These calculations show the well depths (ϵ) differing by an order of magnitude; from 1.0 to 11.9 (x 10^{-5} a.u.). Thus , the experimental data are of particular importance for this system. In a recent experimental investigation of Toennies et al[46], two potentials are reported, which provide equivalent best fits to the measured He-H cross section (ϵ = 1.690 x 10^{-5} and ϵ = 2.536 x 10^{-5}). The more reliable potential is believed to be the one with the smaller well-depth because it best reproduces an observed Ramsauer-Townsend minimum for He-D[46] This potential is in good

agreement with the multiconfiguration-self-consistent-field (MCSCF) results of Das and Wahl[41], but the latest[45] (more elaborate) CI calculation reports a significantly deeper well depth (ϵ = 3.528 x 10^{-5} a.u.) as can be seen in Fig 16. Examining this figure, it is found that our result agrees satisfactorily with the shallower curve which compares well with the previous experiment by Gengenbach and co-workers[47] In the short-range region the present curve agrees very well with all reported theoretical investigations. (There are no experimental results for this region).

The next most investigated system is Ar-H. There are several experimental potentials for this system[39,40,49] in contrast with only one theoretical work done by Wagner et al[48]. The experimental result of Aquilanti[49] does not agree well with the theoretical work while those of Bickes[40] and more recently Bassi[39] are in good accord with the theoretical report of Wagner. In this work, our predicted potential parameters agree within experimental error with Bassi, Bickes and the theoretical work of Wagner.

For the Ne-H case, the only ab initio calculation performed by Bondybey and co-workers[42] has no potential minimum. Other than this, no published theoretical or experimental studies have been done for Ne-H and Kr-H systems. In the summary of results shown in Table 9, the potential parameters ϵ and R_m available for these systems were taken from G. Wolf (private communication) from the paper of Tang and Toennies[24].

It should be noted that our results for the well-studied systems (He-H and Ar-H) are in good agreement with the most reliable

experimental results, despite our dispersive coefficients having a limited accuracy. It is gratifying that our results are also in reasonable agreement with experiment for the other systems (Ne-H and Kr-H) which have yet to be subject to extensive theoretical or experimental investigations.

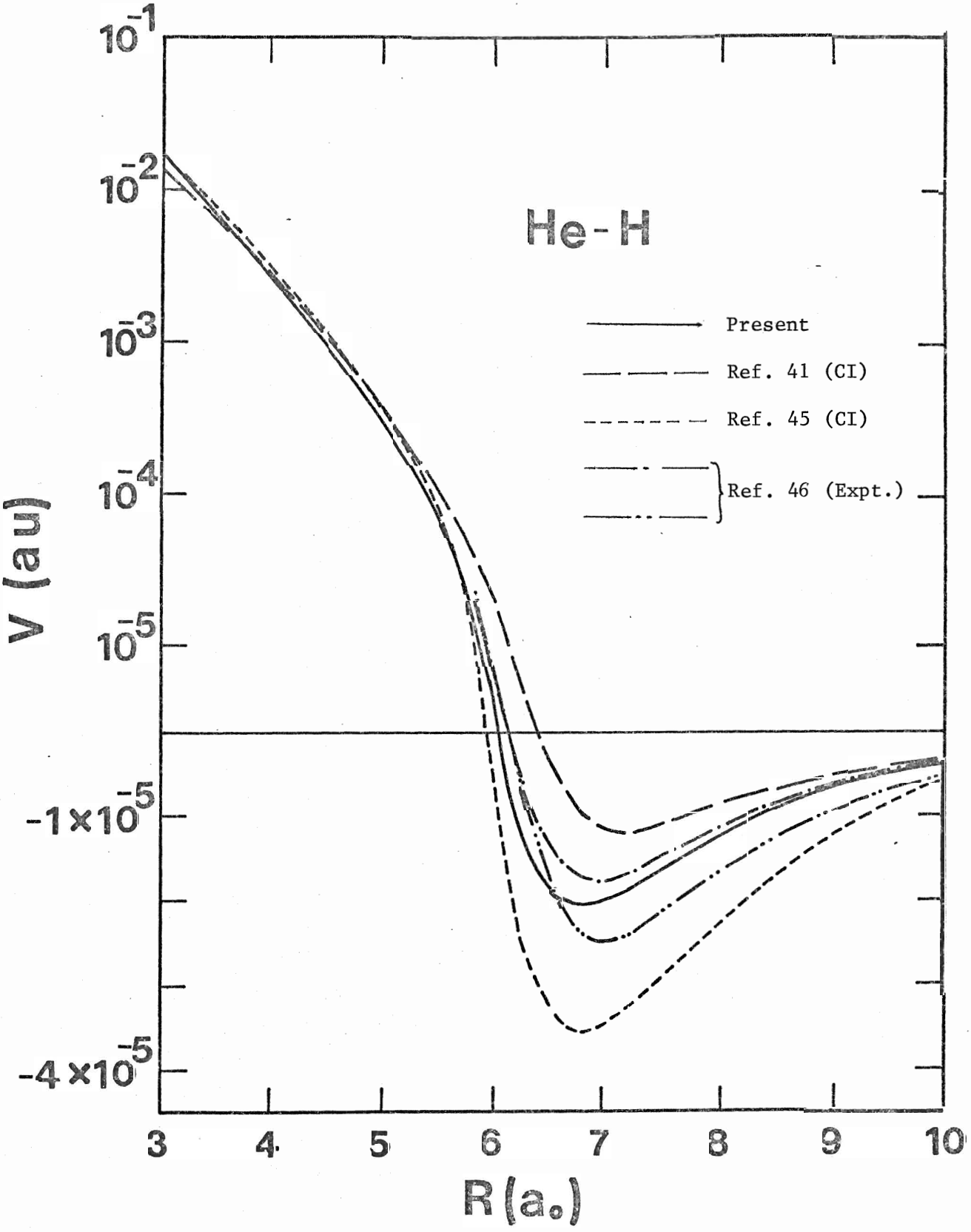

Fig. 16. Interaction potential for He-H ($^2\Sigma^+$).

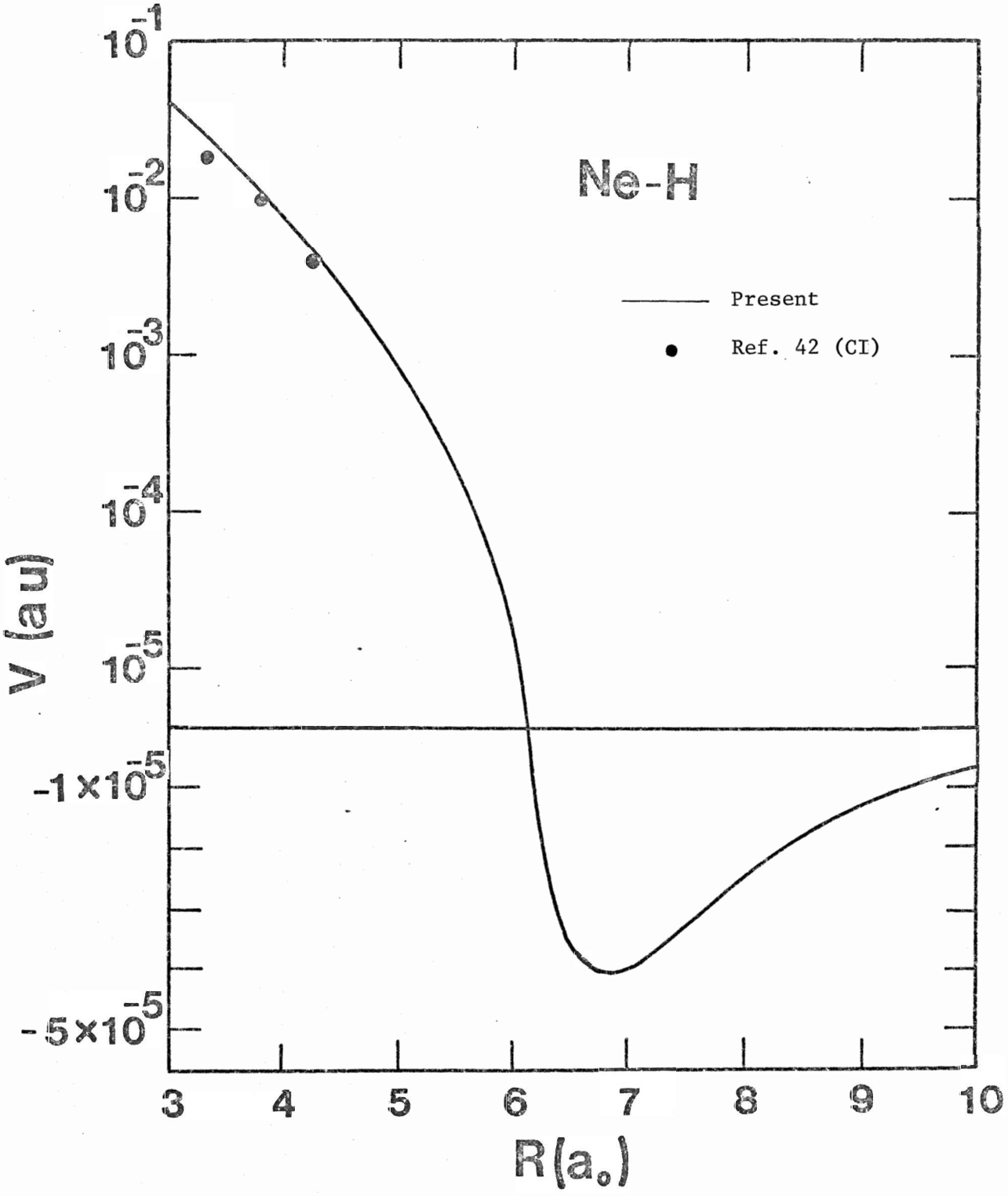

Fig. 17. Interaction potential for Ne-H ($^2\Sigma^+$)

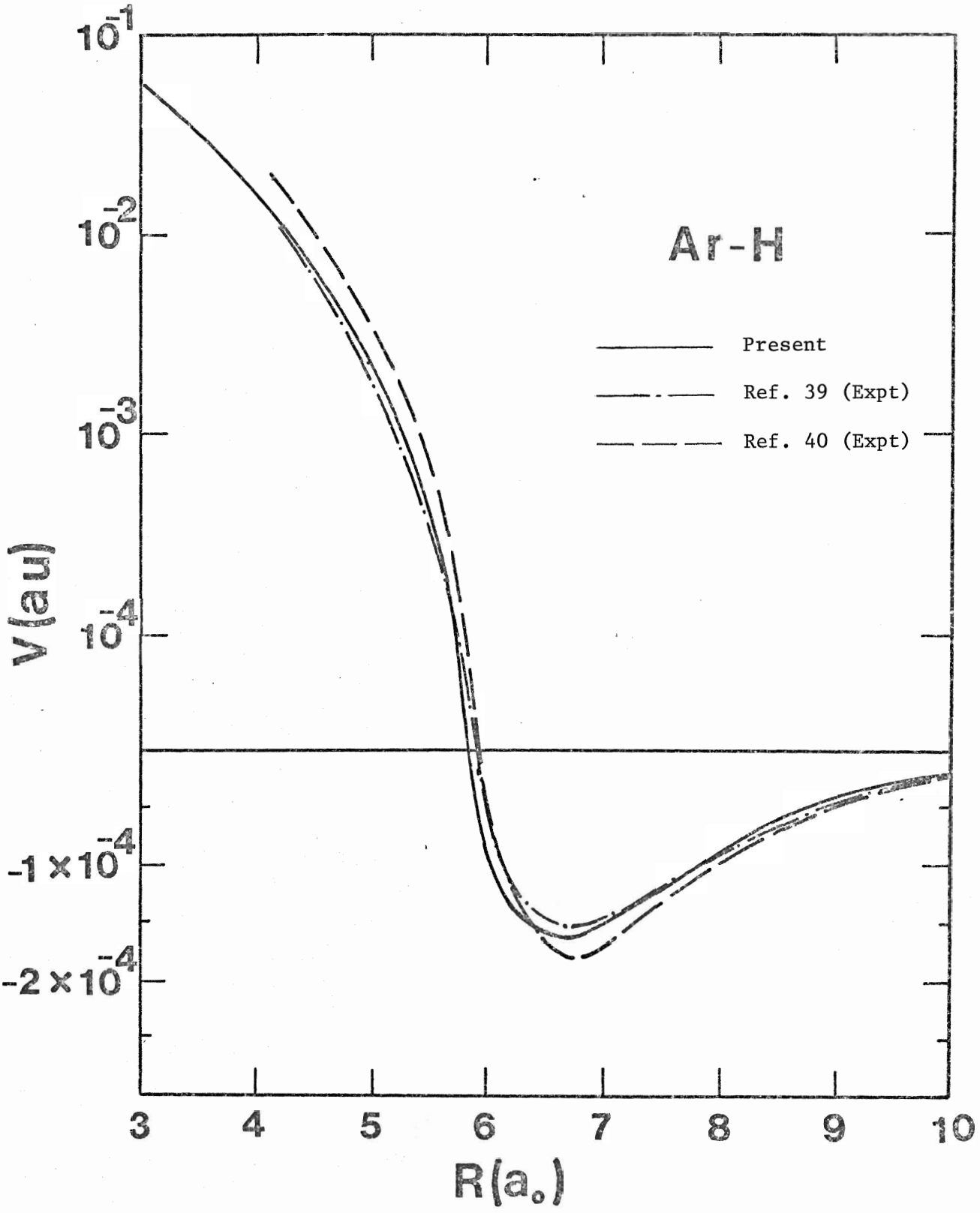

Fig. 18. Interaction potential for Ar-H ($^2\Sigma^+$).

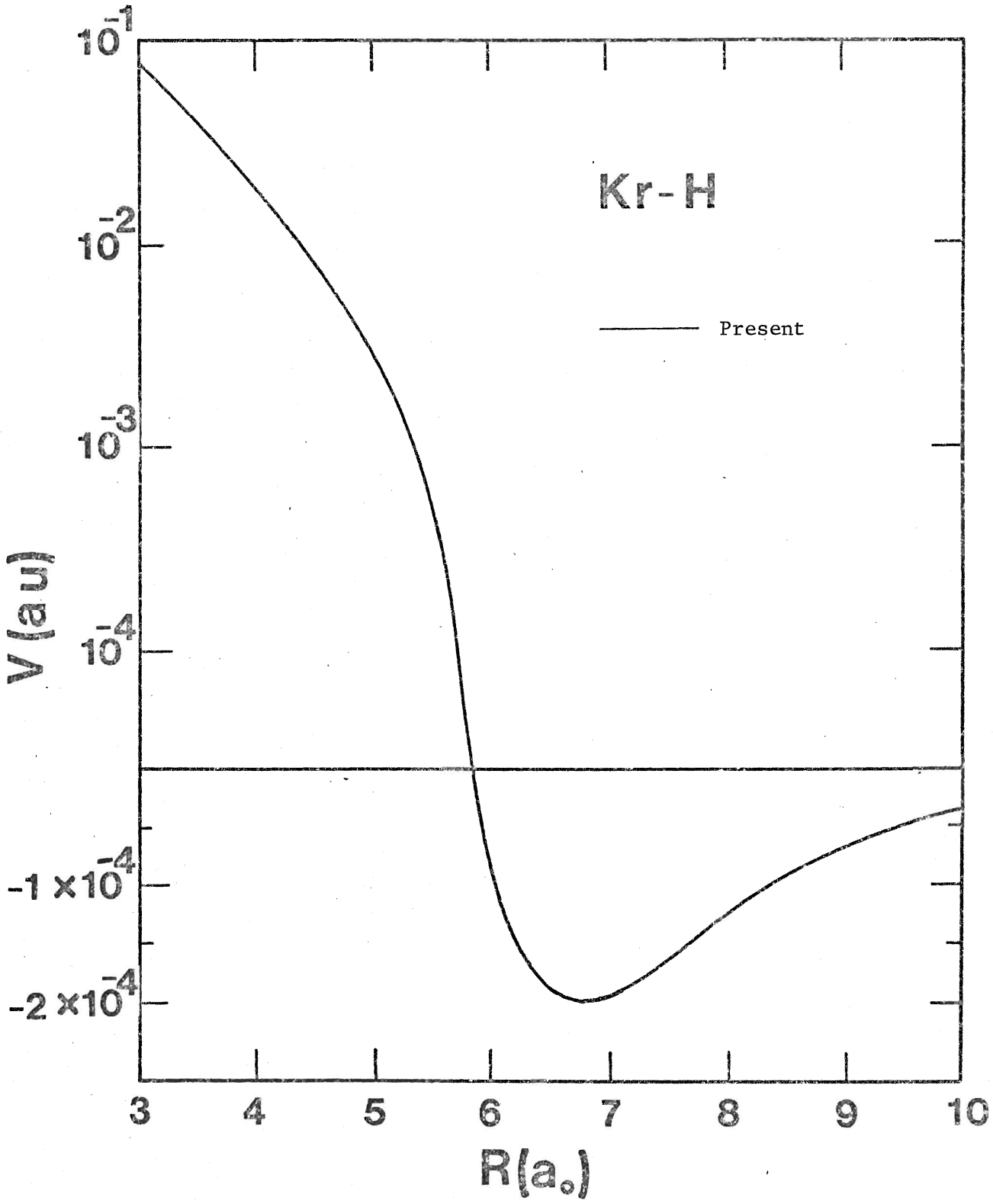

Fig. 19. Interaction potential for Kr-H ($^2\Sigma^+$).

Table 9. Potential parameters for noble gas-Hydrogen interactions.[a]

System	ϵ (x 10^5)	R_m	σ	Reference
He-H	2.02	6.80	6.05	This work
	1.10	7.24	6.60	41 (CI)
	1.69	7.03	6.16	43 (CI)
	11.91	6.56	5.40	44 (CI)
	3.53	6.80	5.93	45 (CI)
	1.69	7.03	6.16	46 (expt)
	2.54	7.03	6.16	46 (expt)
Ar-H	16.31	6.62	5.85	This work
	15.29	6.75	5.86	48 (CI)
	13.08	7.56	6.73	49 (expt)
	15.25	6.84	5.95	39 (expt)
	17.38	6.69	5.95	40 (expt)
Ne-H	4.10	6.83	6.14	This work
	3.57±0.5	6.06±0.7	---	b
	no minimum found			42 (CI)
Kr-H	20.23	6.73	5.86	This work
	21.68±0.4	6.75±0.9	---	b

[a] All values are in atomic units.

[b] G. Wolf (private communication) as quoted by Tang and Toennies.[24]

CHAPTER V

SUMMARY AND DISCUSSIONS

In this thesis, the present modification of the statistical method for determining the intermolecular forces for Van der Waals molecules was discussed, together with the competing statistical methods due to Rae, and Cohen and Pack. It was found out that our method is more accurate in the calculation of the potentials for the pairs of rare gases, He to Kr. In the case of the interaction of Hydrogen atom with the noble gases (He to Kr), the theory satisfactorily predicted the potential parameters ϵ, σ and R_m. Overall, our approach, given accurate dispersive coefficients, could predict quite accurately the form of the potential curve for $R \geq R_m/2$.

The apparent success of our method is due to the different form of exchange density functional employed, the modification of the short-range correlation energy functional and the inclusion of the dispersive energy. The sum of all of these constitute E_Λ^S the 'total correlation'. The exchange energy functional that arises by requiring a Hermitian single particle density matrix in the Thomas-Fermi theory, was found by Handler. The optimized values of α and β, in our correlation energy expression (II-31), were obtained by the use of the minimization subroutine VA04A by Powell[50], employing the correlation energy for He (Table 3), while the dispersive coefficients were taken from Tang et al.[25] and Rae.[8]

It has been noted by Rae[8] from the theory of plasma oscillations[51], that the long-range correlation part of the correlation energy

for the electron gas has a small dispersive contribution. This would account for the following significant observation; the free-electron gas approximation to the correlation energy for the free atoms is too large. This is because the plasma oscillation model includes a dispersive energy which is absent in atoms. Our scheme to parameterize on the He atom removes this contribution. On application to diatoms, we avoid double-counting when the dispersion energy is included.

At very short separation ($R < R_m/2$), all the statistical models fail because of the following;

(i) breakdown in the assumption of additivity of the atomic densities brought about by a distortion of electron clouds due to the displacement of the charged clouds as the atoms come closer together, and

(ii) non-uniformity of the electron distribution in the shells closer to the nucleus, where the electrons are rapidly varying. These causes could perhaps be circumvented by scaling the total density and by curve-fitting the true kinetic energy of the atom concerned and thereby obtaining a functional for the system in question. These are not done because there will be many parameters to deal with, rendering the method uneconomical and obscuring the theoretical foundation.

Exact agreement of our result with experiments in the short and intermediate region could be attained by adjusting the dispersive coefficients within their bounds. As in the work of Cohen and Pack, however, this was not done because it was felt that such empiricism is not necessary due to the difficulties mentioned before.

With the simple, economical and reliable method at hand, it would be worthwhile to apply the present approach to other Van der Waals systems where good ab-initio and accurate experimental findings are not available to date. This certainly would be an important tool in predicting the potential shape and parameters.

A P P E N D I C E S

A P P E N D I X A

DERIVATION OF THE COULOMBIC INTERACTION BETWEEN TWO NEUTRAL ATOMS X AND Y

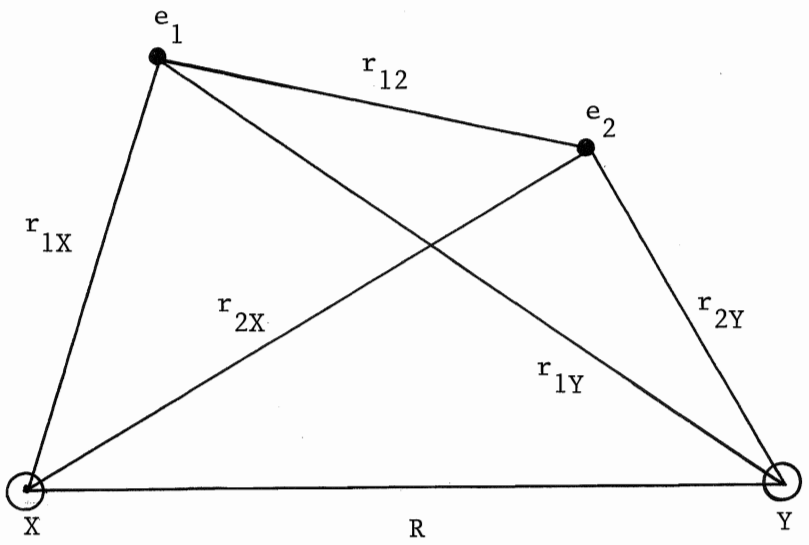

Fig. A-1

From the principal assumption of additive atomic densities (II-4) the total Coulombic energy of atoms X and Y is given by

$$E_c^{(XY)} = V_{XY} + V_{ee} + V_{eX} + V_{eY} \qquad \text{(A-1)}$$

where

$$V_{XY} = Z_X Z_Y / R \quad , \qquad \text{(A-2)}$$

$$V_{ee} = (1/2)\iint [\rho_X(\vec{r}_1) + \rho_Y(\vec{r}_1)]\ [\rho_X(\vec{r}_2) + \rho_Y(\vec{r}_2)]/r_{12}\ d\vec{r}_1 d\vec{r}_2 \ , \qquad \text{(A-3)}$$

$$V_{eX} = -Z_X \int [\rho_X(\vec{r}_1) + \rho_Y(\vec{r}_1)](1/r_{1X})\, d\vec{r}_1 \ , \qquad \text{(A-4)}$$

and

$$V_{eY} = -Z_Y \int [\rho_X(\vec{r}_1) + \rho_Y(\vec{r}_1)](1/r_{1Y})\, d\vec{r}_1 \ . \qquad \text{(A-5)}$$

Equation (A-2) represents the repulsion between nuclei, (A-3) gives the repulsion between the electrons (the factor of 1/2 takes care of the double counting of electron-electron repulsion; i.e., repulsion between electron 1 and electron 2 and repulsion between electron 2 and electron 1 have been counted as one). Equations (A-4) and (A-5) include the attractions between the nuclei and the electrons.

In the above equations, R represents the internuclear distance; Z_X and Z_Y, the nuclear charges; r_{12} the electron-electron distance; and r_{1X} and r_{1Y} the electron-nuclear distances. (see Fig. A-1)

Now, for isolated atoms X and Y, the Coulombic energies are similarly given by

$$E_c^{(X)} = (1/2)\iint [\rho_X(\vec{r}_1)\rho_X(\vec{r}_2)]\ (1/r_{12})\ d\vec{r}_1 d\vec{r}_2 - Z_X \int [\rho_X(\vec{r}_1)](1/r_{1X})\, d\vec{r}_1 \qquad \text{(A-6)}$$

and

$$E_c^{(Y)} = (1/2)\iint [\rho_Y(\vec{r}_1)\rho_Y(\vec{r}_2)](1/r_{12})\ d\vec{r}_1 d\vec{r}_2 - Z_Y \int [\rho_Y(\vec{r}_1)](1/r_{1Y}) d\vec{r}_1 \qquad \text{(A-7)}$$

where the first term in (A-6) and (A-7) gives the electron-electron repulsion and the second term is the electron-nuclear attraction.

The Coulombic interaction energy is then obtained by subtracting the atomic from the total energy.

$$V_c = E_c^{(XY)} - E_c^{(X)} - E_c^{(Y)} \tag{A-8}$$

Substituting (A-1) - (A-7) to (A-8) and simplifying, the following expression results

$$V_c = Z_X Z_Y/R + \iint [\rho_X(\vec{r}_1)\rho_Y(\vec{r}_2)](1/r_{12})\, d\vec{r}_1 d\vec{r}_2 - Z_X \int [\rho_Y(\vec{r}_1)] (1/r_{1X})\, d\vec{r}_1 - Z_Y \int [\rho_X(\vec{r}_1)](1/r_{1Y})\, d\vec{r}_1 \tag{A-9}$$

where

$$\rho_X(\vec{r}_1)\rho_Y(\vec{r}_2) = \rho_X(\vec{r}_2)\rho_Y(\vec{r}_1) \tag{A-10}$$

is used in arriving at the second term in (A-9) ($\vec{r}_1$ and $\vec{r}_2$ are just dummy variables).

Since ,

$$Z_X = \int \rho_X(\vec{r}_1)\, d\vec{r}_1 \tag{A-11}$$

$$Z_Y = \int \rho_Y(\vec{r}_1)\, d\vec{r}_1 \tag{A-12}$$

for neutral atoms, further reduction of (A-9) can be made,

$$V_c = \iint \rho_X(\vec{r}_1)\rho_Y(\vec{r}_2)\, (1/R + 1/r_{12} + 1/r_{1X} + 1/r_{2Y})\, d\vec{r}_1 d\vec{r}_2 \tag{A-13}$$

By incorporating the Coulombic interaction in one integrand, errors due to differences of relatively large and separately integrated terms are reduced[6].

In spherical polar coordinates (A-13) becomes

$$V_c = \int_0^\infty \rho_X(r_1) r_1^2 dr_1 \int_0^\infty \rho_Y(r_2) r_2^2 dr_2 \int_0^{2\pi} d\phi_1 \int_0^{2\pi} d\phi_2 \int_0^\pi \sin\theta_1 d\theta_1$$
$$\int_0^\pi \sin\theta_2 d\theta_2 (1/R + 1/r_{12} + 1/r_{1X} + 1/r_{2Y}) \qquad \text{(A-14)}$$

Angular integrations could now be carried out analytically. It should be noted that the densities are spherically symmetric for closed-shell atoms and therefore are independent of all angles

$$\langle 1/R \rangle = \int_0^{2\pi} d\phi_1 \int_0^{2\pi} d\phi_2 \int_0^\pi \sin\theta_1 d\theta_1 \int_0^\pi \sin\theta_2 d\theta_2 \ (1/R)$$
$$= (4\pi)^2/R \qquad \text{(A-15)}$$

$$\langle 1/r_{1X} \rangle = \int_0^{2\pi} d\phi_1 \int_0^{2\pi} d\phi_2 \int_0^\pi \sin\theta_1 d\theta_1 \int_0^\pi \sin\theta_2 d\theta_2 \ (1/r_{1X})$$
$$= 2(4\pi)^2/(R+r_1+|R-r_1|) \qquad \text{(A-16)}$$

$$\langle 1/r_{2Y} \rangle = \int_0^{2\pi} d\phi_1 \int_0^{2\pi} d\phi_2 \int_0^\pi \sin\theta_1 d\theta_1 \int_0^\pi \sin\theta_2 d\theta_2 \ (1/r_{2Y})$$
$$= 2(4\pi)^2/(R+r_2+|R-r_2|) \qquad \text{(A-17)}$$

$$\langle 1/r_{12} \rangle = \int_0^{2\pi} d\phi_1 \int_0^{2\pi} d\phi_2 \int_0^\pi \sin\theta_1 d\theta_1 \int_0^\pi \sin\theta_2 d\theta_2 \ (1/r_{12})$$
$$= (4\pi)^2 \ F(R,r_1,r_2) \qquad \text{(A-18)}$$

where

$$F(R,r_1,r_2) = 2/(R+r_1+|R-r_1|) \text{ for } r_2 < |R-r_1| \qquad \text{(A-18a)}$$
$$= (1/r_1 + 1/r_2)/2 - R/4r_1r_2 - (r_1-r_2)^2/4Rr_1r_2$$
$$\text{for } |R-r_1| < r_2 < (R+r_1) \ , \qquad \text{(A-18b)}$$

$$= 1/r_2 \quad \text{for } r_2 > R+r_1 \text{ .}^{53} \tag{A-18c}$$

From (A-14) to (A-18), the Coulombic interaction energy can be written as

$$V_c = 16\pi^2 \int_0^\infty \rho_X(r_1) r_1^2 dr_1 \int_0^\infty \rho_Y(r_2) r_2^2 dr_2 \; I$$

where for the homonuclear case,

$$I = 1/R + F(R,r_1,r_2) - 4/(R+r_1+|R-r_1|) \tag{A-20}$$

and for the heteronuclear case,

$$I = 1/R + F(R,r_1,r_2) - 2/(R+r_1+|R-r_1|) - 2/(R+r_2+|R-r_2|). \tag{A-21}$$

A P P E N D I X B

DERIVATION OF THE KINETIC ENERGY EXPRESSION

In 1928, Sommerfeld first applied quantum mechanics to the electron in metals. He simplified the problem by taking the potential energy of each electron to be constant within the metal. In other words, if we assume that the metal is in the form of a cube of side L, and we have non-interacting particles inside, the potential inside is zero and outside the metal may be taken as infinite. Thus, from this idealized situation, the normalized wave functions of the stationary states neglecting spin are

$$\psi_{n_x n_y n_z} = (8/L^3)^{1/2}\left[\sin(n_x \pi x/L)\sin(n_y \pi y/L)\sin(n_z \pi z/L)\right] \quad \text{(B-1)}$$

$$\text{for} \quad 0 < x < L$$

$$0 < y < L$$

$$0 < z < L$$

and

$$\psi_{n_x n_y n_z} = 0 \qquad \text{anywhere else .} \quad \text{(B-2)}$$

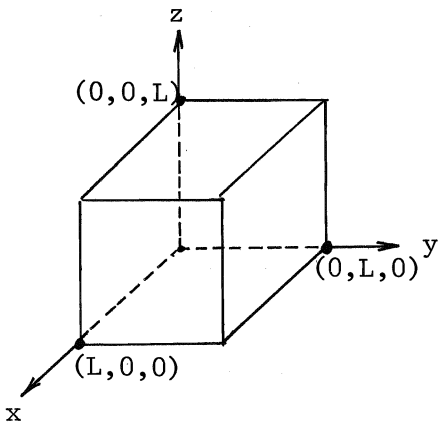

Fig. B-1

The energy levels for this particle in a box model are easily verified as

$$\varepsilon_{n_x n_y n_z} = (\pi^2 / 2L^2)\ (n_x^2 + n_y^2 + n_z^2) \qquad \text{(B-3)}$$

where n_x, n_y and n_z are positive integers.[54]

In our case, it is useful to define a density of states in energy $\mathcal{N}(\varepsilon)$, where the number of orbital states with energies lying between ε and $\varepsilon + d\varepsilon$ is $\mathcal{N}(\varepsilon)d\varepsilon$. From here we can define $\upsilon(\varepsilon)$ as the number of orbital states, with energies less than ε as

$$\upsilon(\varepsilon) = \int_0^{\varepsilon} \mathcal{N}(\varepsilon)d\varepsilon \qquad \text{(B-4)}$$

so that

$$\mathcal{N}(\varepsilon) = d\upsilon/d\varepsilon \ . \qquad \text{(B-5)}$$

Now, to be able to calculate (B-4) and consequently (B-5), we begin by considering a system of rectangular cartesian coordinates whose axes are n_x, n_y and n_z. (see figure B-2)

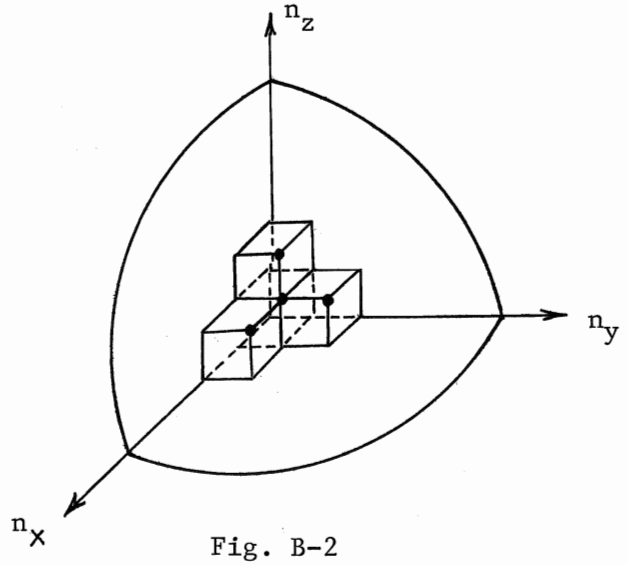

Fig. B-2

It can be noted from the above figure that each orbital state is represented by three positive integral values corresponding to n_x, n_y and n_z respectively. If the octant of this 'n-space' is divided into unit cubic cells as in Fig. B-2, every point representing a state lies in the corner of the cell, and each cell contains one orbital state. In our example the four orbital states are (1,1,1),(1,0,0),(0, 1,0) and (0,0,1).

If we rearrange (B-3) in a way such that

$$n_x^2 + n_y^2 + n_z^2 = 2L^2\varepsilon/\pi^2 \quad , \tag{B-6}$$

it is evident that the right hand side of the above expression is just the square of the radius representing the octant. Therefore, the number of states $\upsilon(\varepsilon)$ with energies less than ε is just the number of points (as in the Fig. B-2) lying within the positive octant of the sphere. Since there is one point per unit volume, $\upsilon(\varepsilon)$ is equal to the volume of the octant, i.e.,

$$\begin{aligned} \upsilon(\varepsilon) &= (1/8)(4\pi/3)(2L^2\varepsilon/\pi^2)^{3/2} \\ &= (L^3/6\pi^2)(2)^{3/2}(\varepsilon)^{3/2}. \end{aligned} \tag{B-7}$$

Differentiating (B-7) with respect to ε gives the density of states ,

$$\mathcal{N}(\varepsilon) = (L^3/4\pi^2)(2)^{3/2}(\varepsilon)^{1/2}. \tag{B-8}$$

At 0°K, two electrons with opposite spin (Pauli principle) will occupy the ground state, two into each state of higher energy and so

on . If we denote the state with maximum energy as ζ_o, and N as the total number of electrons in the system, then we have

$$N = 2\int_0^{\zeta_o} \mathcal{N}(\varepsilon)d\varepsilon \ . \qquad \text{(B-9)}$$

Substituting (B-8) to (B-9) and integrating we will get

$$N = (L^3/2\pi^2)(2)^{3/2}(2/3)\ \zeta_o^{3/2} \ , \qquad \text{(B-10)}$$

which will give , ζ_o, the highest occupied energy level as

$$\zeta_o = (1/2)(3\pi^2 N/L^3)^{2/3} \ . \qquad \text{(B-11)}$$

Since it was assumed that the potential energy is zero within the metal, all the energy is kinetic and ζ_o is the maximum kinetic energy at absolute zero of temperature. The total kinetic energy of the electrons is then

$$2\int_0^{\zeta_o} \mathcal{N}(\varepsilon)\varepsilon d\varepsilon = (L^3/2\pi^2)(2)^{3/2}(2/5)\ \zeta_o^{5/2}$$

$$= 3N\zeta_o/5 \qquad \text{(B-12)}$$

and the average kinetic energy per electron (the Fermi energy) is

$$\varepsilon_k = 3/5\ \zeta_o \ . \qquad \text{(B-13)}$$

Using the result of (B-11) in the above expression and noting that N/L^3 is just the electron density ρ , the expression of the kinetic energy as a function of ρ , will then be

$$\varepsilon_k = (3/10)(3\pi^2)^{2/3}\ \rho^{2/3} \ , \qquad \text{(B-14)}$$

which is our desired result.

Equation (B-14) could also be arrived at by the use of the Hartree's model, wherein the electrons are assumed to interact. To be of use in our case however, it is necessary to introduce a uniform distribution of positive charge that would be just sufficient to neutralize the effect of electron charge. With this viewpoint, the Hartree's equation will simply be

$$(-\nabla^2/2)\psi = \varepsilon\psi \quad . \tag{B-15}$$

The above expression will hold in a free electron gas model , if we would apply a periodic boundary condition with running waves, such that the Hartree potential is zero. Although this periodicity is not physically justifiable in our model of the metal being a cube of side L, we still can get the correct density of states. As pointed out by Raimes - the real justification of the periodicity is that it leads to the correct density of states.(see Ref. 51, p. 164)

A very convenient function representing running waves is of the type

$$\psi_{\vec{k}}(\vec{r}) = Ce^{i\vec{k}\cdot\vec{r}} \tag{B-16}$$

where

$$\vec{k} = k_1\vec{e}_1 + k_2\vec{e}_2 + k_3\vec{e}_3 \tag{B-17}$$

$$\vec{r} = x\vec{e}_1 + y\vec{e}_2 + z\vec{e}_3 \tag{B-18}$$

C is the normalization constant and $\vec{e}_1$, $\vec{e}_2$ and $\vec{e}_3$ are unit vectors directed orthogonally in the cube edges. Applying now (B-16) to (B-15),

$$-(\nabla^2/2)Ce^{i\vec{k}\cdot\vec{r}} = -(\nabla^2/2)Ce^{i(k_1x + k_2y + k_3z)} \qquad \text{(B-19a)}$$

since,

$$\vec{k}\cdot\vec{r} = k_1x + k_2y + k_3z \qquad \text{(vector product)} \qquad \text{(B-20)}$$

and so,

$$-(\nabla^2/2)Ce^{i\vec{k}\cdot\vec{r}} = -(1/2)(k_1^2 + k_2^2 + k_3^2)Ce^{i(k_1x + k_2y + k_3z)} \qquad \text{(B-19b)}$$

$$= -(1/2)k^2Ce^{i\vec{k}\cdot\vec{r}}. \qquad \text{(B-19c)}$$

Since we require our wave function to be triply periodic, i.e.,

$$\psi_k(x+L,y,z) = \psi_k(x,y+L,z) = \psi_k(x,y,z+L) = \psi_k(x,y,z) \qquad \text{(B-21)}$$

then,

$$e^{ik_1L} = e^{ik_2L} = e^{ik_3L} = 1 \qquad \text{(B-22)}$$

such that,

$$k_1 = 2\pi n_1/L \quad , \; k_2 = 2\pi n_2/L \quad , \; k_3 = 2\pi n_3/L \qquad \text{(B-23)}$$

where n_1 , n_2 and n_3 may be positive, negative or zero in this case. From the above reasoning the energy level is

$$\varepsilon(k) = k^2/2 = (1/2)(k_1^2 + k_2^2 + k_3^2) \qquad \text{(B-24)}$$

in '$\vec{k}$-space' , and

$$\varepsilon(k) = (2\pi^2/L^2)(n_1^2 + n_2^2 + n_3^2) \qquad \text{(B-25)}$$

in '$\vec{n}$-space'.

Normalizing the wave function we will have

$$\begin{aligned} 1 &= \int |\psi_{\vec{k}}|^2 \, d\vec{r} \\ &= C^2 \int d\vec{r} \\ &= C^2 L^3 \end{aligned} \tag{B-26}$$

giving C the normalization constant the value of $(1/L^3)^{1/2}$.

Following the same procedure((B-4) to (B-14)), we will find that $\upsilon(\varepsilon)$ will have the same value as (B-7), if we use (B-16) instead of (B-1) and (B-25) instead of (B-3). It should be noted here that the number of states with energies less than ε is equal to the volume of the sphere with radius of $(\varepsilon L^2/2\pi^2)^{1/2}$. Consequently, we will arrive with the same expression of the kinetic energy (B-14).

Equation (B-23), shows us that points in '$\vec{k}$-space' with coordinates $(2\pi n_1/L \, , \, 2\pi n_2/L \, , \, 2\pi n_3/L)$, represent orbital states, and a cube of side $2\pi/L$ therefore contains one orbital state. It can be stated therefore that for a metal of volume L^3, the number of orbital states lying within a volume element $d\vec{k}$ of '$\vec{k}$-space' is $L^3 d\vec{k}/8\pi^3$.

A P P E N D I X C

DERIVATION OF THE EXCHANGE ENERGY EXPRESSION FROM THE ELECTRON GAS MODEL

If we apply the concept of a free electron gas to the Hartree-Fock method, the nuclear-elctron attraction and the electron-electron repulsion terms would vanish since we require the Hartree field to be zero in our model.[51] Hence, in our case the Hartree-Fock equation would be

$$\left[-\nabla^2/2 - \sum_j^N \left(\int \psi_j^*(\vec{r}_2)\psi_i(\vec{r}_2)\psi_j(\vec{r}_1)\{1/(r_{12}\psi_i(\vec{r}_1))\}\, d\vec{r}_2 \right) \right] \times \psi_i(\vec{r}_1) = \varepsilon_i \psi_i(\vec{r}_1) \qquad \text{(C-1)}$$

where the first term is the kinetic energy operator and the second term is the exchange energy operator. The exchange operator has no simple physical interpretation but it arises from the requirement that the wave function be antisymmetric with respect to electron exchange. For our case, we will employ the function described in (B-16) where the normalization constant is equal to $(1/L^3)^{1/2}$, i.e.,

$$\psi_{\vec{k}}(\vec{r}) = (1/L^{3/2})e^{i\vec{k}\cdot\vec{r}} \qquad \text{(C-2)}$$

To be consistent, we will use in (C-1) the subscripts $\vec{k}$ and $\vec{k}'$ to distinguish between eigenfunctions, in place of i and j respectively.

Since the kinetic energy term has been dealt with in Appendix B (by Hartree's method), we will only be concerned with the exchange operator which can be defined by using (C-2) as

$$\varepsilon_x(\vec{k}) = \sum_{k'}\left[\int \psi^*_{\vec{k}'}(\vec{r}_2)\psi_{\vec{k}}(\vec{r}_2)\psi_{\vec{k}'}(\vec{r}_1)\ 1/(r_{12}\psi_{\vec{k}}(\vec{r}_1))\ d\vec{r}_2\right] \qquad \text{(C-3)}$$

Substituting (C-2) to (C-3) and rearranging, we have

$$\varepsilon_x(\vec{k}) = -(1/L^3)\sum_{k'}\left[\int e^{i(\vec{k}-\vec{k}')\cdot(\vec{r}_2-\vec{r}_1)}\ (1/r_{12})\ dr_2\right] . \qquad \text{(C-4)}$$

The integral in (C-4) may be written as

$$I = e^{-i(\vec{k}-\vec{k}')\cdot\vec{r}_1}\int e^{i(\vec{k}-\vec{k}')\cdot\vec{r}_2}\ (1/r_{12})\ d\vec{r}_2 \quad . \qquad \text{(C-5)}$$

To evaluate this expression, we suppose that $\phi(\vec{r})$ is the potential at the point $\vec{r}$ due to a distribution of charge whose density is given by the function $e^{i(\vec{k}-\vec{k}')\cdot\vec{r}}$. (Although this function is not a physical real distribution, for our purpose, it can be treated as such.) Then, $\phi(\vec{r})$ must satisfy Poisson's equation

$$\nabla^2\phi(\vec{r}) = -4\pi e^{i(\vec{k}-\vec{k}')\cdot\vec{r}} \qquad \text{(C-6)}$$

and the required solution, as can be verified by substitution, is

$$\phi(\vec{r}) = 4\pi e^{i(\vec{k}-\vec{k}')\cdot\vec{r}}/|\vec{k}-\vec{k}'|^2 \quad . \qquad \text{(C-7)}$$

Accordingly, the potential at point $\vec{r}_1$, which is

$$\phi(\vec{r}_1) = \int e^{i(\vec{k}-\vec{k}')\cdot\vec{r}_2}\ (1/r_{12})\ d\vec{r}_2 \qquad \text{(C-8)}$$

must, from (C-7), have the value

$$\phi(\vec{r}_1) = 4\pi e^{i(\vec{k}-\vec{k}')\cdot\vec{r}_1}\ /|\vec{k}-\vec{k}'|^2 \quad . \qquad \text{(C-9)}$$

Using (C-8) and (C-9) in (C-5) we arrive at

$$I = 4\pi/|\vec{k}-\vec{k}'|^2 \quad . \tag{C-10}$$

By the use of (C-5) and (C-10), equation (C-4) becomes

$$\varepsilon_x(\vec{k}) = -(4\pi/L^3)\left[\sum_{\vec{k}} \{1/|\vec{k}-\vec{k}'|^2\}\right] \quad . \tag{C-11}$$

To evaluate the above expression, the concept of '$\vec{k}$-space', which has been discussed in appendix B, is necessary. The sum in (C-11) can be replaced by an integral knowing the fact that the volume element $d\vec{k}$ of '$\vec{k}$-space' contains $(L^3/8\pi^3)d\vec{k}$ orbital states.

$$\varepsilon_x(\vec{k}) = -(1/2\pi^2)\int (1/|\vec{k}-\vec{k}'|^2)\, d\vec{k}' \tag{C-12}$$

In spherical polar coordinates (k',θ,ϕ), where θ is the angle between $\vec{k}'$ and $\vec{k}$ (see Fig. C-1), we will find that

$$\begin{aligned}\varepsilon_x(\vec{k}) &= -(1/2\pi^2)\int_0^{k_o} dk' \int_0^{2\pi} d\phi \int_0^{\pi} k'^2 \sin\theta\, (1/|\vec{k}-\vec{k}'|^2)\, d\theta \\ &= -(1/\pi)\int_0^{k_o} dk' \int_{-1}^{1} k'^2 (k^2 + k'^2 - 2kk'\cos\theta)^{-1} d(\cos\theta) \\ &= -(1/\pi k)\int_0^{k_o} k' \log\left|\frac{k+k'}{k-k'}\right| dk' \end{aligned} \tag{C-13}$$

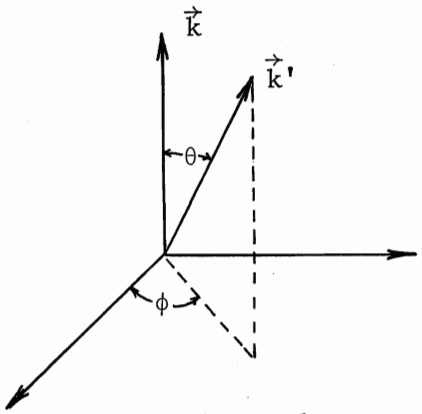

Fig. C-1

From the calculus, it is easily shown by integration by parts, that the following relations hold;

$$\int z^n \log z \, dz = (z^{n+1}/[n+1]) \log z - z^{n+1}/(n+1)^2$$

where n is an integer and $n \neq -1$ (C-14)

$$\int \log z \, dz = z \log z - z \, . \qquad \text{(C-15)}$$

Using the above relations, the result of (C-13) would be

$$\varepsilon_x(\vec{k}) = -(k_o/2\pi) \left[2 + \{(k_o^2 - k^2)/kk_o\} \log \left| \frac{k_o + k}{k_o - k} \right| \right] \, . \qquad \text{(C-16)}$$

It should be noted that k_o in (C-13) and (C-16) pertains to the radius of the sphere, herewith called the Fermi sphere, which encompasses the occupied region in '$\vec{k}$-space' at the absolute zero of temperature. Knowing that each orbital state is occupied by two electrons, therefore, twice the number of states should equal the total number of electrons, i.e.,

$$2(L^3/8\pi^3)(4\pi/3)k_o^3 = N \qquad \text{(C-17)}$$

and solving for k we get,

$$k_o = (3\pi^2 N/L^3)^{1/3} \, . \qquad \text{(C-18)}$$

From the Hartree-Fock model of the free electron gas (C-1), the total energy is not simply obtained by summing the eigenvalues (kinetic plus exchange) over all electrons, which has the result of including the total exchange energy twice. Instead, the total energy is given by

$$2 \sum_{\vec{k}} (k^2/2) + 2 \sum_{\vec{k}} \varepsilon_x(\vec{k}) + \sum_{\vec{k}} \sum_{\vec{k}} \iint \psi^*_k(\vec{r}_1)\psi^*_{k'}(\vec{r}_2)\psi_k(\vec{r}_2)\psi_{k'}(\vec{r}_1)$$

$$(\ \|\ \text{spins})$$

$$[\ 1/r_{12}\ ]\ d\vec{r}_1 d\vec{r}_2 \qquad \text{(C-19)}$$

where the first term is the total kinetic energy and the sum of the second and last term is the total exchange energy. Using (C-13) and simplifying, the total exchange energy becomes

$$V_e(\vec{k}) = \sum_{\vec{k}} \varepsilon_x(\vec{k}) \qquad \text{(C-20)}$$

and the average exchange energy (per electron) is just

$$\varepsilon_e(\vec{k}) = (1/N) \sum_{\vec{k}} \varepsilon_x(\vec{k}) \quad . \qquad \text{(C-21)}$$

Substituting (C-16) to (C-21) and replacing the sum by an integral, (C-21) can now be evaluated to give

$$\varepsilon_e(\vec{k}) = -(L^3/16\pi^4 N)\int_0^{k_o} [2k_o + \{(k_o^2 - k^2)/k\}\log\left|\frac{k_o + k}{k_o + k}\right|\ ]\ 4\pi k^2 dk$$

$$\varepsilon_e(\vec{k}) = -(L^3/4\pi^3 N)\ k_o^4 \quad . \qquad \text{(C-22)}$$

Substituting (C-18) for k_o in the above expression and noting that the density is N/L^3, we will have

$$\varepsilon_e(\rho) = -(1/4\pi^3)\ (L^3/N)\ (3\pi^2\{N/L^3\})^{4/3}$$

$$= -(3/4)\ (3/\pi)^{1/3}\ \rho^{1/3} \qquad \text{(C-23)}$$

which is the desired result.

In the theory of plasma oscillations in metals, it was noted by Raimes[51] that the exchange energy is very much exaggerated in the Hartree-Fock model of the free-electron gas. This fact has been noted in the work of Gordon and Kim[6] and subsequent workers[8,9]. Raimes said that the difficulty would be overcome if the long-range Coulomb correlation is taken into account before applying the Pauli principle. The result of his derivation, which will not be given here (see Reference 51, p.294) is

$$\varepsilon_e(\text{Raimes};\rho,\beta) = \varepsilon_e(\rho)\ [\ 1 - 4\beta/3 + \beta^2/2 - \beta^4/48\ ] \qquad \text{(C-24)}$$

where the dimensionless quantity β, is not exactly known. For sodium atom, Raimes value of β is 0.8 while Pines' value is 0.7[55]. Recently, Rae[8] chose β such that the 'self-exchange' contribution can be eliminated. His β, is the solution of

$$N = (N^2/2)\ (\beta^3 - 9\beta^4/16 + \beta^6/32) \qquad \text{(C-25)}$$

where N is the number of electrons involved. Discrepancies, however, arise as to what constitutes N. For example, Lloyd and Pugh[56] suggested taking N as the number of the outer shell electrons instead of the total number of electrons.

A P P E N D I X D

HANDLER'S EXCHANGE ENERGY EXPRESSION

We begin by defining a single particle density matrix $\rho(11')$, and the two particle density matrix $\rho(12,1'2')$ as

$$\rho(11') = (2/N-1)\int d\vec{r}_2 \rho(12,1'2') \tag{D-1}$$

$$\rho(12,1'2') = N(N-1)/2 \int d\vec{r}_3 \ldots d\vec{r}_N \, \psi^*(\vec{r}_1', \vec{r}_2', \vec{r}_3, \ldots, \vec{r}_N)\psi(\vec{r}_1, \ldots \vec{r}_N) \tag{D-2}$$

where N is the number of particles and ψ is the wave function.

If the wave function for the system is a single determinant, (D-2), could be written as

$$\bar{\rho}(12,1'2') = c\begin{vmatrix} \rho(11') & \rho(12') \\ \rho(21') & \rho(22') \end{vmatrix}$$

$$= c[\rho(11')\rho(22') - \rho(12')\rho(21')] \quad . \tag{D-3}$$

It should be noted that (D-1) and (D-3) contain spin coordinates. Since we are dealing with space coordinates, these expressions could be written as, assuming equal spin up and spin down densities,

$$\rho(11') = \rho_s(11')[\alpha(1)\alpha^*(1') + \beta(1)\beta^*(1')]$$

$$= \rho_s(11')\sigma(11') \quad . \tag{D-4}$$

Correspondingly,

$$\bar{\rho}(12,1'2') = c[\rho_s(11')\rho_s(22')\sigma(11')\sigma(22') - \rho_s(12')\rho_s(21')\sigma(12')$$

$$\sigma(21')] \qquad \text{(D-5)}$$

where the subscript s indicates a function of space coordinates only. Normalizing would result to

$$\mathrm{Tr}\rho_s(11') = N/2 \qquad \text{(D-6)}$$

$$\begin{aligned}\mathrm{Tr}\rho_s(12,1'2') &= c[4(N/2)^2 - 2\mathrm{Tr}\rho_s(12')\rho_s(21')] \\ &= c[4(N/2)^2 - 2\mathrm{Tr}\rho_s(11')] \\ &= c(N^2 - N) \qquad \text{(D-7)}\end{aligned}$$

where c as in (D-3) would have the value of 1/2.

In Hartree-Fock theory, the two-particle property is the inter-electronic potential energy operator $1/|\vec{r}_1 - \vec{r}_2|$.

$$\begin{aligned}V^e &= \mathrm{Tr}[1/|\vec{r}_1-\vec{r}_2|\rho(12,1'2')] \\ &= \mathrm{Tr}\{1/|\vec{r}_1-\vec{r}_2|(1/2)\ [4\rho_s(11')\rho_s(22') - 2\rho_s(12')\rho_s(21')]\} \\ &= (1/2)\{4\int d\vec{r}_1\rho_s(11')\ d\vec{r}_2\rho_s(22')/|\vec{r}_1-\vec{r}_2| \ - 2\int d\vec{r}_1\rho_s(11') \\ &\qquad (1/\rho_s(11'))\int d\vec{r}_2[\rho_s(12)]^2/|\vec{r}_1-\vec{r}_2|\} \\ &= \mathrm{Tr}\ [V_c^e\ (\vec{r}_1) + V_E^e\ (\vec{r}_1)]\rho_s(11') \quad . \qquad \text{(D-8)}\end{aligned}$$

As traditionally formulated , the single particle density matrix can be written as (spin-free)

$$\rho_s(11') = \psi_n^*(\vec{r}_1')\theta\ (\lambda_N - H)\psi_n(\vec{r}_1) \qquad \text{(D-9)}$$

where

$$\theta(y) = 1 \quad , y > 0$$
$$\theta(y) = 0 \quad , y < 0 \qquad \text{(D-10)}$$

and the λ_N is a constant fixed by normalization.

In classical theory, the Hamiltonian H can be partitioned to kinetic and potential energy operators (T + V). Applying the concept of '$\vec{k}$-space' and using the wavefunction in (C-2) with the normalization constant equal to $1/L^{3/2}$, (D-9) becomes

$$\rho_s(11') = \sum_{\vec{k}} \psi_k^*(\vec{r}_1')\, \theta(y) \psi_k(\vec{r}_1) \quad . \qquad \text{(D-11)}$$

For the case, $\theta(y) = 1$, we will have from (D-11)

$$\rho_s(11') = \sum_{\vec{k}} \psi_k^*(\vec{r}_1')\psi_k(\vec{r}_1)$$
$$= (1/L^3) \sum_{\vec{k}} e^{i\vec{k}\cdot(\vec{r}_1-\vec{r}_1')} \quad . \qquad \text{(D-12)}$$

Replacing the sum by an integral throughout the occupied '$\vec{k}$-space',

$$\rho_s(11') = (1/L^3)(L^3/8\pi^3) \int e^{i\vec{k}\cdot(\vec{r}_1-\vec{r}_1')}\, d\vec{k}$$
$$= (1/8\pi^3) \int e^{i\vec{k}\cdot(\vec{r}_1-\vec{r}_1')}\, d\vec{k} \qquad \text{(D-13)}$$

In order to evaluate the above integral, we employ the spherical coordinate system (k,ϕ,θ), where the θ is the angle between $|\vec{r}_1-\vec{r}_1'|$ and $\vec{k}$ as shown in Fig. (D-1). Thus (D-13) becomes

$$\rho_s(11') = (1/8\pi^3) \int_0^{k_o} \int_0^{2\pi} \int_0^{\pi} e^{i\vec{k}\cdot(\vec{r}_1-\vec{r}_1')}\, k^2 dk d\phi \sin\theta d\theta$$
$$= (1/4\pi^2) \int_0^{k_o} \int_{-1}^{1} e^{i\vec{k}\cdot(\vec{r}_1-\vec{r}_1')}\, k^2\, d(\cos\theta)\, dk$$

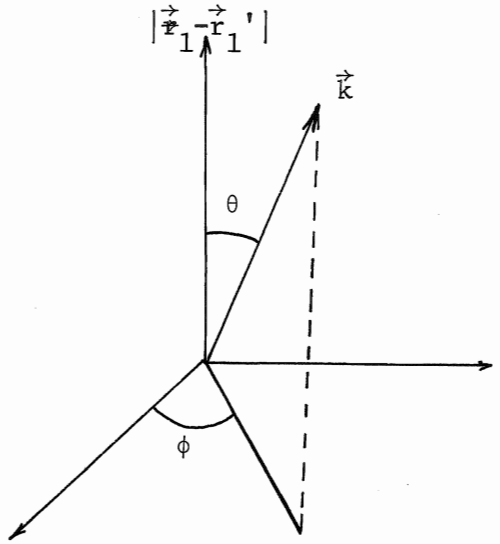

Fig. (D-1)

$$= (1/4\pi^2)\int_0^{K_o}\int_{-1}^{1} e^{ikr_{12}\cos\theta}\ k^2 d(\cos\theta)\ dk$$

$$= (1/4\pi^2)\int_0^{K_o} [\ (1/ikr_{12})\ \{e^{ikr_{12}} - e^{-ikr_{12}}\}\ ]\ k^2 dk \qquad (D\text{-}14)$$

Now,

$$\sin x = (e^{ix} - e^{-ix})/2i$$

$$\rho_s(11') = (1/4\pi^2)\int_0^{K_o} (2/kr_{12})\ \sin(kr_{12})\ k^2 dk$$

$$= (1/2\pi^2)\int_0^{K_o} k\ \sin(kr_{12})\{\ 1/r_{12}\}\ dk$$

$$= (1/2\pi^2)\ [\ \sin\ (k_o r_{12}) - k_o r_{12}\cos\ (k_o r_{12})]/r_{12}^3 \qquad (D\text{-}15)$$

The form of k_o depends on the system one is considering. For example, for systems with Coulomb interaction,

$$k_o = 2(\lambda_N - [z\phi(r)/r])^{1/2} \qquad (D\text{-}16)$$

where ϕ is a shielding function which is found by imposing a condition of self-consistency, together with a suitable boundary condition in the form of a Poisson equation[57]

$$\nabla^2 V(r) = -4\pi\rho_s(r) \quad . \tag{D-17}$$

The above equation has been solved numerically by Kobayashi et al.[58] to yield ϕ for the general atomic problem.

If we substitute $\rho_s(11')$ to (D-8), using the proper exchange operator as defined in (C-3), we will come up with the usual expression for exchange energy as being proportional to $\rho^{1/3}$. (see Appendix C)

The major flaw in the above procedure lies in the fact that we have assumed that $\rho_s(11')$ is Hermitian, in going from (D-1) to (D-8), which is not necessarily the case when V(r) is not a constant given the form of k_o. To correct the situation, King and Thomas[59] replaced r in (D-16) with

$$\xi = [(1+b)r_> + (1+b)r_<]/2 \tag{D-18}$$

where $r_>$ and $r_<$ refer to the greater or lesser of r_1 and r_1'. This has the effect of generating a range of possible Hermitian density matrices, depending on the value of b.

King and Thomas studied the effect of altering the form of ξ on the kinetic, Coulombic and exchange energy. They found out that the exchange energy is the only one altered by the change in the form of ξ.

Subsequently, Handler[10], calculated the exchange energy operator from $\bar{\rho}_s(12,1'2')$. Thus from (D-15) and (D-8), the exchange opera-

tor becomes

$$V_E^e(r_1) = (2\pi/\rho_s(11)) \left[\int_0^{r_1} dr_2 \int_0^{r} d\alpha + \int_{r_1}^{\infty} dr_2 \int_0^{r} d\alpha \right] [\rho_s(12)]^2 \times (1/|\vec{r}_1-\vec{r}_2|)\, r_2^2 \sin\alpha \qquad \text{(D-19)}$$

where $\cos\alpha = \vec{r}_1 \cdot \vec{r}_2/(r_1 r_2)$. The value of k required to evaluate $\rho_s(12)$ is determined by the lesser of $[k_o(1), k_o(2)]$. This is equivalent to setting b=1 in (D-18).

The complicated expression in (D-19) has been numerically treated by Handler. Handler's formula as given on page 4827 of Ref. 10, is a fit to (D-19), which he integrated numerically. Unfortunately, the fit is not uniformally good as the expression he obtained tends to pass through a maximum at large ρ rather than levelling off. To correct this he subsequently modified his expression[18]. The new version is given in (II-25) of the main text.

The most important difference of (D-19) from the traditional expression lies in the fact that at large r (small ρ), the exchange operator is drastically reduced such that the limiting law of $\sim\rho^{2/3}$ instead of $\sim\rho^{1/3}$, is found.

APPENDIX E

DISCUSSION OF CORRELATION ENERGY

For a free electron gas, the correlation energy is more difficult to evaluate than any of the other energy terms. Several attempts have been made[19,20,55,60-63], and agreement among the various results is satisfactory. In this section, the correlation expressions evaluated by different authors, are discussed.

1. Correlation energy at very low densities.

In the free electron gas approximation, the atomic radius r_s can be defined as

$$4\pi r_s^3/3 = L^3/N$$

$$r_s = (3/4\pi\rho)^{1/3} \qquad \text{(E-1)}$$

The kinetic and exchange functional in (B-14) and (C-23) could then be expressed in terms of the atomic radius r_s as

$$\varepsilon_k(r_s) = 1.105/r_s^2 \qquad \text{(E-2)}$$

$$\varepsilon_e(r_s) = -0.458/r_s \qquad \text{(E-3)}$$

We can see from (E-2) that as r_s increases (lower densities), the kinetic energy would be very small and finally tend to form a stable lattice. In such event, the total energy may be calculated using the atomic sphere approximation.[51] From this model, it may be viewed that the energy per electron at very low densities will approximately equal that of an electron at the center of a uniform spherical distribution of posi-

tive charge, of radius r_s, and charge of +1 (in atomic units). The density of positive charge is therefore equal to $3/(4\pi r_s^3)$. Suppose that an electron is at the center of a sphere, of radius r, of positive charge density, the total charge within the sphere is

$$\text{Total charge} = -1 + (4\pi r^3/3)(3/4\pi r_s^3)$$

$$= -1 + r^3/r_s^3 \qquad \text{(E-4)}$$

and the potential at the surface of the sphere would be

$$V(r) = [-1 + r^3/r_s^3](1/r) \quad . \qquad \text{(E-5)}$$

The energy required to bring a shell of positive charge, of thickness dr from infinity is

$$E(r) = V(r)\ (3/4\pi r_s^3)\ (4\pi r^2 dr) \ . \qquad \text{(E-6)}$$

Substituting (E-5) to (E-6) and simplifying we will have

$$E(r) = (3/r_s^3)[(r^3/r_s^3) - 1]\ r dr \qquad \text{(E-7)}$$

The energy per electron at very low densities is therefore

$$\varepsilon_t^{\ell} = (3/r_s^3) \int_0^{r_s} [(r^3/r_s^3) - 1]\ r\ dr \quad . \qquad \text{(E-8)}$$

Upon integration we will obtain

$$\varepsilon_t^{\ell} = -0.9/r_s \qquad \text{(E-9)}$$

Since the kinetic energy is zero at very low densities, the Hartree-Fock energy would just be that due to exchange energy of the electrons.

Hence, the correlation energy per electron at large r_s is

$$\varepsilon^{\ell}_{corr} = -0.9/r_s - (-0.458/r_s)$$

$$= -0.442/r_s \quad . \qquad \text{(E-10)}$$

Fuchs[60], who considered a body-centered cubic lattice of electrons, obtained a value of $-0.891/r_s$ for the first term in (E-10). Higher order approximations are obtained from the analysis of the zero-point motion of electrons about their lattice points (a body-centered cubic lattice of electrons is usually considered). In the low density region, therefore, the calculation involves the evaluation of the normal modes of oscillations. Two independent calculations have been made[61, 62] which agree to within one per cent; the average value of the two being 1.325 $r_s^{-3/2}$. In 1961, Carr et al.[20] , calculated the third term representing (E-9) by evaluating the first anharmonic contribution to the ground state energy of the bcc (body-centered cubic) lattice of electrons oscillating in a uniform background of positive charge. Their result is $-0.365\ r_s^{-2}$.

Basically, a complete solution of lattice dynamics is obtained by expanding the Coulomb potential in powers of displacements of the electrons about their respective lattice points. The energy is therefore an infinite series in powers of $r_s^{-1/2}$, the terms beyond $r_s^{-3/2}$ are the anharmonic corrections, which can be calculated from the perturbation theory.

With the use of the results of various authors[60-62] and their own work[19], Carr et al.[20] give the correlation energy for dilute electron

gas as

$$\varepsilon_{corr}^{\ell} = 0.438\ r_s^{-1} + 1.325\ r_s^{-3/2} - 1.47\ r_s^{-2} - 0.4\ r_s^{-5/2}$$

$$r_s \geq 10 \quad . \qquad \text{(E-11)}$$

2. Correlation energy at high densities.

A straightforward perturbation calculation is the only way to tackle the correlation energy of an electron gas at small r_s (high densities). In 1957, Gell-Mann and Brueckner[63], made a calculation of the correlation energy, which they claim to be very accurate at high density limit,

$$\varepsilon_{corr}^{h}(GB;r_s) = 0.0311 \log r_s - 0.048 + O(r_s) \ , \qquad \text{(E-12)}$$

the last term being small and goes to zero with r_s. Subsequently, Carr and Maradudin[19] made an estimate of $O(r_s)$ on the same line of calculation as Gell-Mann and Brueckner. They come up with,

$$\varepsilon_{corr}^{h} = 0.0311 \log r_s - 0.048 + 0.009\ r_s \log r_s - 0.01 r_s$$

$$r_s \leq 0.7 \quad . \qquad \text{(E-13)}$$

Many more calculations of the correlation energy for the free electron gas have been done based upon the perturbation theory of infinite order. Most of them are in good agreement with the later work of Carr and Maradudin[19] and Carr et al.[20]

3. Other developments.

Perturbation calculations are valid only on high and low densi-

ty limits, so that in order to obtain from them the correlation energy at actual metallic densities, it is necessary to interpolate between the two limits. Wigner[30] obtained the earliest interpolation formula,

$$\varepsilon_{corr}^{i} = -0.44/(r_s+7.8) \quad , \tag{E-14}$$

and recently , Gordon and Kim[6] employed a logarithmic interpolation formula as

$$\varepsilon_{corr}^{i} = -0.06156 + 0.01898 \log r_s \quad .$$

$$0.7 < r_s < 10. \tag{E-15}$$

In an attempt to find a way to incorporate the high, intermediate and low density expressions into a single functional, McWeeney[29] inspired by the work of Colle and Salvetti[64], suggested an improved method of estimating the correlation energy of an electron gas at all values of r_s. McWeeny starts with an expression for a two-electron correlation function, $\phi(\vec{r}_1,\vec{r}_2)$, which is the form recommended by Colle and Salvetti. After some manipulation, he relates ϕ to a rational function of a single parameter, which for an electron gas is proportional to $\rho^{1/3}$. An expression for the correlation energy

$$E_c = (1/2)\int[\rho_2^{HF}(\vec{r}_1,\vec{r}_2)/r_{12}][\phi^2(\vec{r}_1,\vec{r}_2) - \phi(\vec{r}_1,\vec{r}_2)]\, d\vec{r}_1\, d\vec{r}_2$$

(E-16)

is then evaluated at various values of ρ . McWeeney accurately fits his result over a wide range of density by a single simple formula,

$$\varepsilon_{corr}(\text{McW};\ ) = -[9.652 + 2.946\ \rho^{-1/3}]^{-1}. \qquad \text{(E-17)}$$

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